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Protonation of Diarylacetylenes in Superacid HSO_3F and Their Oxidation in the HSO_3F/PbO_2 System: One-Pot Synthesis of Polysubstituted Naphthalenes

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In the superacid HSO_3F, diarylacetylenes bearing one electron-withdrawing group (NO_2, CN, COMe, CO_2Me) in each arene ring form stable ions, protonated at these groups. Oxidation of such diarylacetylenes in the HSO_3F/PbO_2 system at –75 to –50 °C over 2–2.5 h, followed by quenching of the reaction mixture with hydrochloric (or hydrobromic) acid at –60 to 25 °C, resulted in the formation of (*E*,*E*)-1,4-dichloro (or dibromo)-1,2,3,4-tetraarylbuta-1,3-dienes. These butadienes spontaneously undergo electrocyclic transformation into polysubstituted naphthalenes at room temperature.

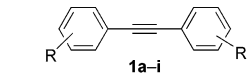
Introduction

Oxidation of alkynes is widely used in organic synthesis.[1,2] One-electron oxidation of acetylene compounds with intermediate formation of acetylene cation radicals affords various valuable multifunctional compounds in one-pot reactions.[3–7]

One of the most efficient oxidants for the generation of organic cation radicals is lead dioxide (PbO_2) in acidic media.[8] The $CF_3CO_2H/CH_2Cl_2/PbO_2$ system has been successfully utilised for the preparative oxidation of different acetylene derivatives.[4–6] The main limitation of this oxidative system is the impossibility of achieving cation radical formation of deactivated diarylacetylenes bearing strongly electron-withdrawing substituents (NO_2, CN, COMe, CO_2Me, etc.), due to their high oxidative potentials.[4] The use of stronger acid, in the form of neat hydrogen fluoride, results in the production of cation radicals of such deactivated diarylacetylenes, which in the HF/PbO_2 system leads to the formation of 1,4-difluoro-1,2,3,4-tetraarylbuta-1,3-dienes.[7] In our recent preliminary communication we demonstrated in principle the use of superacid HSO_3F along with PbO_2 for the one-electron oxidation of 1,2-bis(4-acetylphenyl)acetylene.[9]

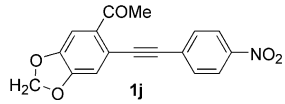
In this report we present data on the protonation of diarylacetylenes bearing strongly electron-withdrawing substituents in the superacid HSO_3F, their one-electron oxidation in the HSO_3F/PbO_2 system and further electrocyclic transformations of their oxidation products.

For this study, we synthesised (Experimental Section) a series of symmetrically substituted compounds, **1a**–**e**, each bearing two electron-withdrawing groups (COMe, CN, NO_2, CO_2Me), polymethyl-substituted dinitro diarylacetylenes **1f**–**h**, compound **1i**, with two dimethylamino groups in both *para* positions in its aromatic rings, and the nonsymmetrical diarylacetylene **1j** (Figure 1).



1a–i

R = 4-COMe (**a**), 4-CN (**b**), 4-NO_2 (**c**), 3-NO_2 (**d**), 4-CO_2Me (**e**), 2,5-Me_2-4-NO_2 (**f**), 2,4,6-Me_3-3-NO_2 (**g**), 2,3,5,6-Me_4-4-NO_2 (**h**), 4-NMe_2 (**i**)



1j

Figure 1. Diarylacetylenes used in this study.

Because of the tremendous protonation capability of superacidic media,[10] triple bonds of rather basic acetylenes may undergo protonation with the formation of extremely reactive vinyl cations, which are further transformed into secondary products.[11–16] Thus, before starting the oxidation of diarylacetylenes in the HSO_3F/PbO_2 system one has to be sure that diarylacetylenes are stable in HSO_3F and that no electrophilic reactions – such as vinyl sulfonate formation,[11,12,15c,15d] dimerisation[11,13,16] or other transformations[14,15a,b,16] – will take place.

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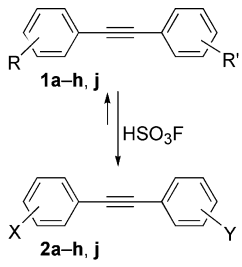
Results and Discussion

NMR spectra of compounds **1a**–**h** and **1j** dissolved in neat HSO_3F at –80 or 0 °C show the formation of stable ions **2a**–**h** and **2j**, fully protonated (or specifically solvated) at their electron-withdrawing groups (Scheme 1). Chemical shifts for the ^1H NMR spectra of ions **2a**–**h** and **2j** in HSO_3F at –80 and at 0 °C are given in Table 1. ^{13}C NMR spectra of ions **2a**–**c**, **2e** and **2f** (HSO_3F, –80 and 0 °C), together with those of their corresponding neutral precursors **1a**–**c**, **1e** and **1f** ($CDCl_3$, 25 °C), are presented in Table 2.



2: X = Y = 4-COH^+Me (**a**); 4-CNH^+ (**b**); 4-NO_2H^+ (**c**); 3-NO_2H^+ (**d**); 4-COH^+OMe (**e**); 2,5-Me_2-4-NO_2H^+ (**f**); 2,4,6-Me_3-3-NO_2H^+ (**g**); 2,3,5,6-Me_4-4-NO_2H^+ (**h**); X = 2-COH^+Me-4,5-OCH_2O, Y = 4-NO_2H^+ (**j**)

Scheme 1. Protonation of diarylacetylenes bearing electron-wihdrawing substituents in the superacid HSO_3F.

Table 1. ^1H NMR spectra of ions **2a**–**h** and **2j** in HSO_3F at –80 and 0 °C.

	T [°C]	Chemical shifts δ [ppm] (spin–spin interaction constants *J*) H arom.	X, Y[a]
2a	–80	8.01 (s, 4 H), 8.56 (s, 4 H)	3.34 (s, 6 H, 2 × Me), 13.39 (s, 2 H, 2 × C=OH^+)
	0	8.03 (d, *J* = 7.5 Hz, 4 H), 8.59 (d, *J* = 7.5 Hz, 4 H)	3.89 (s, 6 H, 2 × Me)
2b[b]	–80	8.00 (d, *J* = 5.7 Hz, 4 H), 8.27 (d, *J* = 5.7 Hz, 4 H)	–
2c	–80	8.09 (s, 4 H), 8.69 (s, 4 H)	–
	0	8.06 (d, *J* = 8.6 Hz, 4 H), 8.64 (d, *J* = 8.6 Hz, 4 H)	–
2d[b]	–80	8.05–8.61 (m, 8 H)	–
2e	–80	7.95 (s, 4 H), 8.23 (s, 4 H)	4.64 (s, 6 H, 2 × MeO), 12.72 (s, 2 H, 2 × C=OH^+)
	0	7.96 (d, *J* = 8.3 Hz, 4 H), 8.25 (d, *J* = 8.3 Hz, 4 H)	4.69 (s, 6 H, 2 × MeO)
2f	–80	7.99 (s, 2 H), 8.88 (s, 2 H)	2.75 (s, 6 H, 2 × Me), 2.77 (s, 6 H, 2 × Me)
	0	7.97 (s, 2 H), 8.83 (s, 2 H)	2.76 (s, 6 H, 2 × Me), 2.81 (s, 6 H, 2 × Me)
2g[b]	–80	7.62 (s, 2 H)	2.81 (s, 12 H, 4 × Me), 3.04 (s, 6 H, 2 × Me)
2h[b]	–80	–	2.26 (s, 12 H, 4 × Me)
2j[b]	–80	7.71 (s, 1 H), 8.14 (d, *J* = 8.7 Hz, 2 H), 8.33 (s, 1 H), 8.83 (d, *J* = 8.7 Hz, 2 H)	3.05 (s, 3 H, MeO), 6.58 (s, 2 H, OCH_2O)

[a] Substituents X and Y are shown in Scheme 1. [b] Unstable at 0 °C.

The proton and carbon spectra clearly demonstrate the exclusive formation of the protonated forms **2a**–**h** and **2j**. No specific signals of products of acetylene transformations in HSO_3F, such as vinyl protons[11,14,15c,15d] or vinyl cationic carbons,[14] could be observed. Diarylacetylenes **1a**–**h** and **1j** do not undergo protonation at the triple bond in HSO_3F at –80 °C. Compounds **1a** and **1e**, with acetyl and methoxycarbonyl groups, form doubly protonated structures **2a** and **2e**, respectively. Their ^1H NMR spectra in HSO_3F at –80 °C contain the corresponding signals of protons attached to oxygen atoms at δ = 13.29 ppm for ion **2a** and at δ = 12.72 ppm for ion **2e** (Table 1). Other acceptors – the nitro groups in compounds **1c**, **1d** and **1f**–**h** and the cyano groups in compound **1b** do not give rise to any definite signals for bonded protons due to fast proton exchange in HSO_3F (compare with our previous NMR observations[15]). Hexa- and octamethyl-substituted substrates **1g** and **1h** give stable ions **2g** and **2h** in HSO_3F at –80 °C, but at higher temperatures protonation of the acetylene triple bonds occurs and secondary reactions take place at 0 °C. The same behaviour is observed for compounds **1b**, **1d** and **1j** (Table 1).

For ^{13}C NMR spectra it is worth mentioning the downfield shifts of the acetylene carbon signals due to the protonation of electron-withdrawing substituents in the aromatic rings. The difference in the chemical shifts of, for instance, the acetylene carbon atoms in neutral precursor **1f** and its protonated form **2f** reaches values of up to Δδ = ca. 9 ppm in HSO_3F at 0 °C (cf. the signals in Table 2).

Upon dissolution of the bis-dimethylamino-substituted diarylacetylene **1i** in HSO_3F at –80 °C, the formation of the diprotonated form of vinyl fluorosulfonate **3** was detectable by ^1H NMR (Scheme 2). The proton spectrum of species **3** contains a broad singlet at δ = 7.44 ppm, corresponding to the overlapped signals of the vinyl proton and two protons of the protonated dimethylamino groups (Experimental Section). Vinyl fluorosulfonate **3** is formed by addition of HSO_3F to the acetylene bond of the *N*,*N*-diprotonated form of initial **1i**. The addition occurs despite the electron-withdrawing character of the dimethylammonium groups NMe_2H^+, which just slightly deactivate the triple bond towards the protonation. In a preparative-scale experiment in HSO_3F (Experimental Section) diarylacetylene **1i** gives ketone **4** as the product of hydrolysis of vinyl fluorosulfonate **3** (Scheme 2).

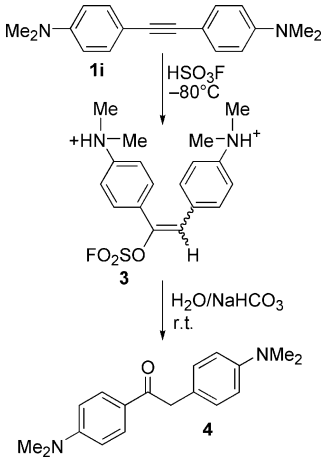
After studying the stability of diarylacetylenes in HSO_3F we carried out preparative oxidation of diarylacetylenes **1a**–**d** in the HSO_3F/PbO_2 system (Scheme 3).

NMR spectra show the complete protonation of the electron-withdrawing substituents in ions **2a**–**d** in HSO_3F (Scheme 1), but nonprotonated compounds **1a**–**d** in equilibrium may undergo one-electron oxidation by PbO_2 in HSO_3F,[17] as shown in Scheme 3. Oxidations of diarylacetylenes **1a**–**d** were carried out for 2–2.5 h at –75 or –50 °C in the HSO_3F/PbO_2 system. Quenching of the superacidic reaction mixtures with frozen concentrated hydrochloric acid at –60 °C then resulted in the formation of (*E*,*E*)-1,4-dichloro-1,2,3,4-tetraarylbuta-1,3-dienes **5a**–**d**.

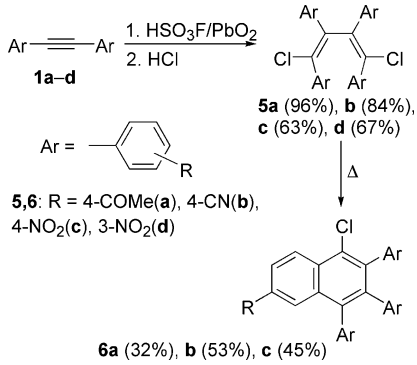
Table 2. ^{13}C NMR spectra of compounds **1a–c**, **1e** and **1f** and their protonated forms **2a–c**, **2e** and **2f**.

	Solvent	*T* [°C]	Chemical shifts δ, ppm (spin–spin interaction constants *J*, Hz)					
			Csp[a]	Aromatic C atoms[b]				R, X, Y[c]
				C-1	C-2 and C-6	C-3 and C-5	C-4	
1a	$CDCl_3$	25[d]	91.6	127.4	131.8	128.3	136.6	197.2 (2×C=O) 26.6 (2×Me)
2a	HSO_3F	–80	97.4 (s)	138.0 (s)	134.1 (d, *J* = 167.7 Hz)	138.2 (d, *J* = 166.5 Hz), 132.9 (d, *J* = 169.3 Hz)[e]	129.3 (s)	219.0 (s, 2×C=OH^+), 25.4 (q, *J* = 131.6 Hz, 2×Me)
		0	98.2 (t, *J* = 4.6 Hz)	139.0 (t, *J* = 8.4 Hz)	134.5 (dd, *J* = 170.1, 5.6 Hz)	135.9 (br. d, *J* = 164.1 Hz)	129.8 (t, *J* = 7.6 Hz)	219.3 (q, *J* = 3.2 Hz, 2×C=OH^+), 25.40 (q, *J* = 132.0 Hz, 2×Me)
1b	$CDCl_3$	25[d]	91.3	126.6	132.0	131.9	112.2	118.0 (2×CN)
2b	HSO_3F	–80[d]	94.4	133.6	136.5	133.8	100.8	107.4 (2×CNH^+)
1c	$CDCl_3$	25[d]	92.0	128.8	132.6	123.8	147.6	–
2c	HSO_3F	–80	93.4 (s)	138.3 (s)	138.3 (d, *J* = 170.5 Hz)	128.6 (d, *J* = 174.1 Hz)	142.5 (t, *J* = 7.4 Hz)	–
		0[d]	99.4	138.0	135.5	128.3	143.7	–
1e	$CDCl_3$	25[d]	91.3	127.3	131.6	129.6	129.9	166.4 (2×C=O) 52.3 (2×MeO)
2e	HSO_3F	–80	94.2 (s)	134.0 (s)	131.9 (d, *J* = 166.1 Hz)	133.7 (d, *J* = 169.7 Hz)	121.6 (s)	181.5 (s, 2×C=OH^+), 63.0 (q, *J* = 154.1 Hz, 2×MeO)
		0[d]	94.9	135.0	132.2	134.0	121.8	182.0 (2×C=OH^+), 63.4 (2×Me)
1f	$CDCl_3$	25[d]	93.8	127.6	139.2 and 136.0	125.62 and 131.1	148.3	20.3 (2×Me), 20.0 (2×Me)
2f	HSO_3F	–80	102.3 (s)	139.2 (s)	143.8 (s) and 138.9 (d, *J* = 170.1 Hz)	130.4 (d, *J* = 171.3 Hz) and 140.3 (s)	144.2 (s)	19.6 (q, *J* = 126.8 Hz, 2×Me), 22.3 (q, *J* = 22.32 Hz, 2×Me)
		0	102.8 (d, *J* = 4.0 Hz)	139.5 (m, *J* = 4.8 Hz)	144.0 (m, *J* = 5.2 Hz) and 139.3 (dm, *J* = 169.3, 4.4 Hz)	130.7 (dm, *J* = 166.5, 4.8 Hz) and 141.4 (t, *J* = 4.8 Hz)	144.2 (m, *J* = 6.8 Hz)	19.8 (q, *J* = 133.6 Hz, 2Me), 22.3 (q, *J* = 133.2 Hz, 2×Me)

[a] Acetylene carbon atoms. [b] Aromatic atom C-1 is the *ipso*-carbon to the acetylene triple bond, other atoms C-2 to C-6 are counted from C-1. [c] Substituents R, X and Y are shown in Schemes 1 and 2. [d] Spectrum with $^{13}C–^{1}H$ decoupling. [e] Two nonequivalent signals due to the protonation of carbonyl group and restricted rotation around bond C-4–C(OH^+)Me (see the same phenomenon in our previous works[15a,15b]).



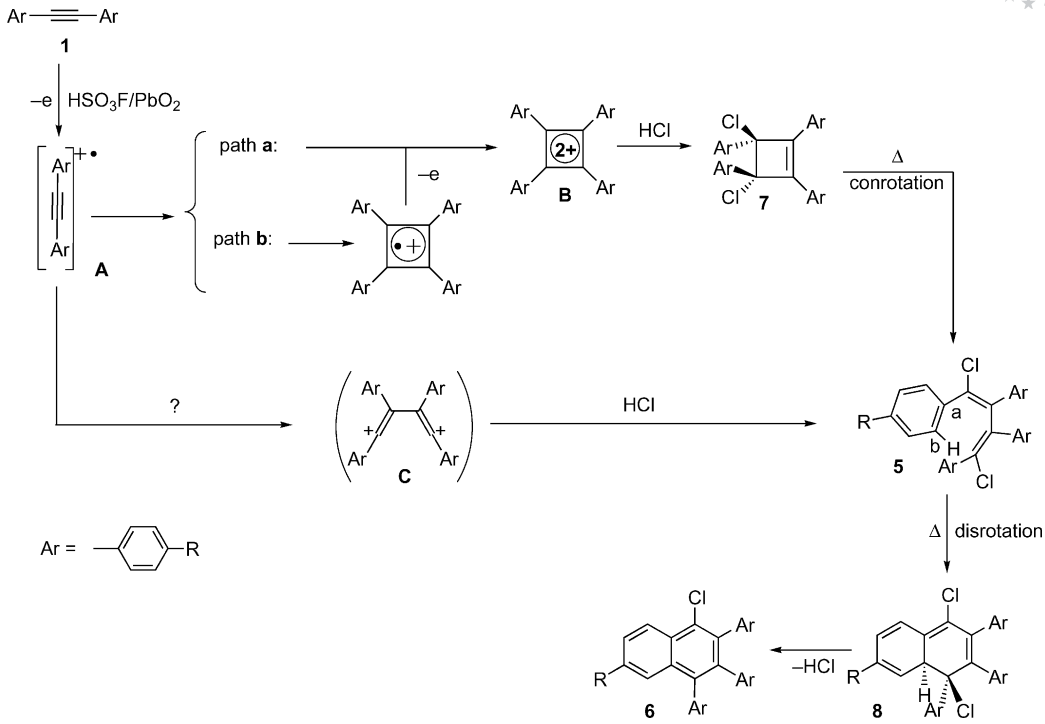
Scheme 2. Formation of vinyl fluorosulfonate **3** and ketone **4** from diarylacetylene **1i**.



Scheme 3. Oxidation of diarylacetylenes **1a–d** in the HSO_3F/PbO_2 system (quenching with HCl) to afford butadienes **5a–d** and further transformations of the latter into naphthalenes **6a–c**.

After storage in air at room temperature, crystalline butadienes **5a–c** became amorphous substances and were slowly transformed into secondary products. After recrystallisation (Experimental Section) these products were found to be substituted naphthalenes **6a–c**. The exact structure of compound **6a** was determined by X-ray diffraction analysis.[9] Periodic monitoring of the ^{1}H NMR spectra of compounds **5a–c** showed their complete conversion into naphthalenes **6a–c** at room temperature in 30–60 d (Experimental Section).

The most plausible mechanism for explaining the formation of compounds **5** and **6** is outlined in Scheme 4. One-



Scheme 4. Mechanism of the formation of butadienes **5a**–**d** and naphthalenes **6a**–**c**.

electron oxidation of substrates **1** into cation radicals **A** may lead to cyclobutadiene dications **B**,[18] which can be formed in two ways: one possible pathway is a cation radical dimerisation (path a) and another is a dimerisation reaction between species **A** and initial **1** followed by one-electron oxidation (path b).[19]

Alternative formation of butadiene dications **C** seems to be unfavourable, especially in the presence of electron-withdrawing groups,[15] as the vinyl cation formation would most probably suffer from a high energetic barrier.[11,13,14] However, our experimental results do not allow us to disregard this reaction pathway entirely.

Previously, stable aromatic dications **B** were obtained from dibromo-substituted cyclobutenes in superacids at low temperature and characterised by NMR spectroscopic methods.[20] In our low-temperature ^{1}H NMR spectroscopic study we tried to generate and directly to observe the formation of dications **B** from the PbO_2 oxidation of compounds **1a** and **1c** dissolved in HSO_3F at –80 or –50 °C in NMR tubes. However, the spectra revealed the formation of complex mixtures. While these samples were stored in NMR tubes at –50 °C for 10 d, regular spectral checking did not show any changes in their ^{1}H NMR spectra. After 10 d storage, the quenching of these special samples with HCl (–60 °C) in the same way as for the preparative reactions (vide supra) led to butadienes **5a** and **5c**. The complex character of the ^{1}H NMR spectra of the oxidation mixtures is strong evidence for the formation of several intermediate species. On one hand, it could be that dication **B** exists in equilibrium with the corresponding fluorosulfonates before solvolysis by HCl to give dichlorocyclobutenes **7**, which easily undergo electrocyclic ring-opening into butadienes **5** in the reaction quenching temperature range between –60 and 25 °C.[21] On the other hand, the possibility that the intermediacy of dication **C** could also lead to the same products by the same solvolysis process cannot be excluded.

Knowing the exact structure of naphthalenes **6**,[9] it is possible to speculate about the electrocyclic transformations of nonisolable cyclobutenes **7** into naphthalenes **6** and to determine the definite stereochemical configurations of compounds **7**, **5** and **8** (Scheme 4) on the basis of symmetry rules.[22]

For the final formation of naphthalenes **6**, cyclobutadienes **7** should possess a *trans* arrangement of substituents in the cyclobutene ring. Under thermal conditions the ring-opening of *trans*-cyclobutadienes **5** is a four-electron conrotatory process,[22] leading to (*E*,*E*)-butadienes **5**. Only butadiene structure **5** with the *E*,*E* configuration[23] has a suitable conformation for further six-electron disrotatory ring closure into compounds **8**. In this electrocyclic reaction the arene C^a=C^b bond of compounds **5** is one of the double bonds of a triene system involved in cyclisation.[24] It is true that pericyclic reactions generally occur at higher temperatures, but with these compounds, never studied before, the strongly electron-withdrawing groups may facilitate the reaction.

At the final step of this transformation a favourable *trans* elimination of an HCl molecule from derivatives **8** occurs, leading to naphthalenes **6**. The driving force of this reaction is the aromatisation into the naphthalene system.

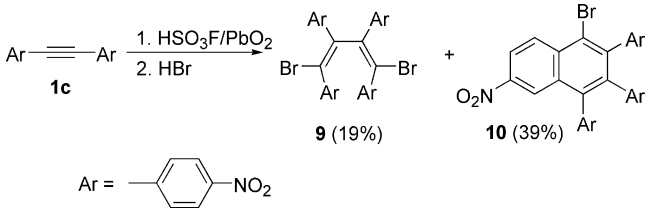
The alternative formation of cyclobutenes **7** with *cis* configuration of substituents must be excluded because in this

case the conrotatory cyclobutene ring-opening should give isomeric (*E*,*Z*)-butadienes **5**,[25] which would exhibit four nonequivalent arene rings in their ^{1}H and ^{13}C NMR spectra. In contrast, the NMR spectra of compounds **5a**–**d** clearly show only two pairs of nonequivalent arene rings (Experimental Section), corresponding to (*E*,*E*)- or (*Z*,*Z*)-butadienes **5**. The (*Z*,*Z*) isomers of **5**, however, do not have any suitable conformation for further thermal electrocyclic transformation into compounds **8**.

It is worth noting the influence of electron-withdrawing substituents R in the aromatic rings of butadienes **5a**–**c** (Scheme 3) on their ring-closure into compounds **8a**–**c** and further conversion into naphthalenes **6a**–**c**. The stronger the acceptor R, the more easily the cyclisation proceeds. Thus, oxidation of acetyl- and cyano-substituted diarylacetylenes **1a** and **1b** gives only butadienes **5a** and **5b** (Scheme 3), which are transformed into naphthalenes **6a** and **6b** in approximately 60 d at room temperature. In contrast, the oxidation of compound **1c**, with more strongly accepting nitro groups,[26] leads to butadiene **5c** in admixture with compound **6c**, which is already formed under the thermal conditions of reaction mixture quenching (–60 to 25 °C). The complete conversion of butadiene **5c** into naphthalene **6c** is achieved in less time (around 30 d) at room temperature (see Experimental Section).

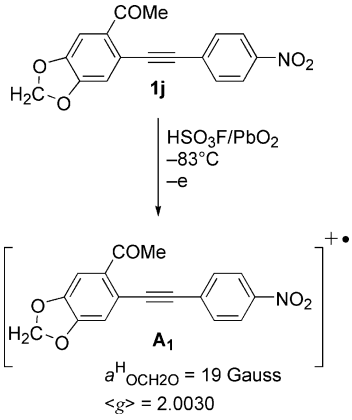
Butadiene **5d**, containing 3-nitrophenyl rings (moderate acceptor[26]), is rather stable. Storage of this compound at room temperature over four months (≈120 d) has not shown any significant transformation into naphthalene **6**.

We have also carried out the oxidation of substrate **1c** in the HSO_3F/PbO_2 system with concentrated hydrobromic acid as a quenching medium. This led to a mixture of dibromo-substituted butadiene **9** together with naphthalene **10** as the major compound, confirming that dibromide **9** was easily transformed into the corresponding naphthalene by electrocyclisation (Scheme 5).



Scheme 5. Oxidation of diarylacetylene **1c** in the HSO_3F/PbO_2 system (quenching with HBr) to afford butadiene **9** and naphthalene **10**.

Intermediate formation of diarylacetylene cation radicals **A** in the HSO_3F/PbO_2 system (Scheme 4) was verified by low-temperature ESR through the generation of cation radical $\mathbf{A_1}$ from compound **1j** (Scheme 6). The ESR spectrum of cation radical $\mathbf{A_1}$ is a triplet with hyperfine splitting constant a^H = 19 G caused by spin interaction of an unpaired electron with two protons of the OCH_2O group.[27]



Scheme 6. Formation and characterisation of cation radical $\mathbf{A_1}$.

Conclusions

In superacid HSO_3F at –80 or 0 °C, diarylacetylenes bearing two powerful electron-withdrawing substituents (NO_2, CN, COMe, CO_2Me) in their aromatic rings form stable ions, which are protosolvated at these electron-withdrawing groups. Such deactivated diarylacetylenes do not undergo any protonation at their acetylene carbon atoms, and no electrophilic reactions occur at the acetylene triple bonds in HSO_3F.

One-electron oxidation of the diarylacetylenes in the HSO_3F/PbO_2 system at –75 to –50 °C in 2–2.5 h with subsequent quenching of the reaction mixtures with concentrated hydrochloric (or hydrobromic) acid results in the formation of (*E*,*E*)-1,4-dichloro-(or dibromo)-1,2,3,4-tetraarylbuta-1,3-dienes. These butadienes are spontaneously electrocyclically transformed into substituted naphthalenes[28] at room temperature.

This work and previous studies have shown the efficiency of cation radical transformations of acetylene compounds in new carbon–carbon bond-forming reactions.[3–7] In these processes the diarylacetylenes can be considered suitable precursors for the synthesis of conjugated butadienes,[7,9] which can be further used for the preparation of polymers, in Diels–Alder chemistry and in other electrocyclic transformations.

Experimental Section

General: ^{1}H and ^{13}C NMR spectra of compounds were recorded with a Bruker AM 500 spectrometer at 500 and 125 MHz, respectively. The residual proton solvent peak $CDCl_3$ (δ = 7.26 ppm) for ^{1}H NMR spectra and the signal of $CDCl_3$ (δ = 77.0 ppm) for ^{13}C NMR spectra were used as references. ^{1}H and ^{13}C NMR experiments in superacid HSO_3F were performed on a Bruker AC 400 spectrometer at 400 and 100 MHz, respectively. NMR spectra in HSO_3F were referenced to the signal of CH_2Cl_2 added as internal standard: δ = 5.32 ppm for ^{1}H NMR spectra, and δ = 53.84 ppm for ^{13}C NMR spectra. Low-resolution mass spectra (electron impact, ionisation energy 70 eV) were obtained with a MKh-1321 machine. ESR spectra in the HSO_3F/PbO_2 system were recorded at 190 K (–83 °C) with a Bruker ESR spectrometer. The preparative

reactions were monitored by thin-layer chromatography carried out on silica gel plates (Silufol UV-254) with use of UV light for detection. Column chromatographic separations were performed on silica gel Chemapol 40/100 (0.04–0.10 mm) with elution with hexane/chloroform mixtures. Diarylacetylenes **1a**–**j** were prepared by our reported procedures.[4a,4b] Synthesis and characteristics of compounds **1a** and **1b**[4b] and **1c**–**f**, **1h** and **1i**[4a] were published previously.

1,2-Bis(2,4,6-trimethyl-3-nitrophenyl)acetylene (1g): This compound was obtained from (2,4,6-trimethyl-3-nitrophenyl)acetylene and 1-iodo-2,4,6-trimethyl-3-nitrobenzene by the reported procedure.[4a,4b] Yield 20%. M.p. 210–213 °C. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 2.29 (s, 6 H, 2 × Me), 2.46 (s, 6 H, 2 × Me), 2.51 (s, 6 H, 2 × Me), 7.04 (s, 2 H, Ar) ppm. MS: *m*/*z* = 352 $[M]^+$. $C_{20}H_{20}N_2O_4$ (352.14): calcd. C 68.17, H 5.72, N 7.95; found C 68.10, H 5.80, N 8.02.

1-(2-Acetyl-4,5-methylenedioxyphenyl)-2-(4-nitrophenyl)acetylene (1j): This compound was obtained from (4-nitrophenyl)acetylene and 1-acethyl-1-iodo-4,5-methylenedioxybenzene by the reported procedure.[4a,4b] Yield 17%. M.p. 179–181 °C. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 2.71 (s, 3 H, Me), 6.08 (s, 2 H, OCH_2O), 6.18 (s, 1 H, Ar), 7.30 (s, 1 H, Ar), 7.66 (d, *J* = 8.9 Hz, 2 H, Ar), 8.22 (d, *J* = 8.9 Hz, 2 H, Ar) ppm. MS: *m*/*z* = 309 $[M]^+$. $C_{17}H_{11}NO_5$ (309.27): calcd. C 66.02, H 3.58, N 4.53; found C 65.98, H 3.63, N 4.58.

Experiments in Superacid HSO_3F: Generation and identification of ions **2a**–**h**, **2j** (Tables 1 and 2) and **3** by NMR in HSO_3F at –80 and 0 °C were carried out by our reported method.[15] **Ion 3**: ^{1}H NMR (400 MHz, HSO_3F, –80 °C): δ = 3.33 (s, 6 H, 2 × Me), 3.38 (s, 6 H, 2 × Me), 7.44 (s, 3 H, =CH, 2 × NH^+), 7.60 (d, *J* = 5.4 Hz, 4 H, Ar), 7.72 (d, *J* = 5.4 Hz, 4 H, Ar) ppm.

1,2-Bis(4-dimethylaminophenyl)ethanone (4): This compound was obtained by the following procedure. Diarylacetylene **1i** (200 mg) was dissolved in HSO_3F (3 mL) at –75 °C (dry ice/acetone bath). After stirring at this temperature for 1 h, the reaction mixture was quenched with an ice/water mixture (≈150 mL) and neutralised with solid $NaHCO_3$. The aqueous phase was extracted with diethyl ether (3 × 50 mL), and the organic layer was washed with saturated $NaHCO_3$ and water and then dried with Na_2SO_4. After solvent evaporation under reduced pressure, the residue was purified by column chromatography. Product **4** was isolated in 45% yield (90 mg). M.p. 200–202 °C. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 2.86 (s, 6 H, 2 × Me), 3.03 (s, 6 H, 2 × Me), 4.02 (s, 2 H, CH_2), 6.66 (d, *J* = 8.5 Hz, 2 H, Ar), 6.70 (d, *J* = 8.8 Hz, 2 H, Ar), 7.11 (d, *J* = 8.5 Hz, 2 H, Ar), 7.90 (d, *J* = 8.8 Hz, 2 H, Ar) ppm. MS: *m*/*z* (%) = 282 (23) $[M]^+$, 148 (100), 134 (45), 118 (12). $C_{18}H_{22}N_2O$ (282.38): calcd. C 76.56, H 7.85, N 9.92; found C 76.59, H 7.90, N 10.01.

General Procedure for Oxidation of Diarylacetylenes 1a–d in the HSO_3F/PbO_2 System: Diarylacetylenes **1a**–**d** (0.75 mmol) were dissolved in HSO_3F (5 mL) at –75 °C (dry ice/acetone bath), and PbO_2 (0.75 mmol) was then added with vigorous magnetic stirring. After stirring at –75 or –50 °C for 2–2.5 h (see below conditions for synthesis of individual compounds), the reaction mixture was quenched with frozen concentrated hydrochloric acid (≈50 mL) at –60 °C. The mixture was diluted with water, and warmed up to room temperature. Solid residue was filtered off, washed with water, and dried in air. Finally, reaction products **5a**–**d** were purified by column chromatography.

(*E*,*E*)-1,2,3,4-Tetrakis(4-acetylphenyl)-1,4-dichlorobuta-1,3-diene (5a): This compound was obtained by the oxidation of diarylacetylene **1a** (178 mg, 0.68 mmol) with PbO_2 (162 mg, 0.68 mmol) in HSO_3F (4 mL) at –50 °C in 2.5 h. Yield 202 mg (96%). Characteristics were published previously.[9]

(*E*,*E*)-1,4-Dichloro-1,2,3,4-tetrakis(4-cyanophenyl)buta-1,3-diene (5b): This compound was obtained by the oxidation of diarylacetylene **1b** (129 mg, 0.57 mmol) with PbO_2 (135 mg, 0.57 mmol) in HSO_3F (4 mL) at –50 °C in 2.5 h. Yield 126 mg (84%). M.p. 178–181 °C (decomp.). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 7.20 (d, *J* = 8.1 Hz, 4 H, Ar), 7.48 (d, *J* = 8.1 Hz, 4 H, Ar), 7.50 (d, *J* = 8.0 Hz, 4 H, Ar), 7.54 (d, *J* = 8.0 Hz, 4 H, Ar) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ = 112.4, 113.0, 117.7, 117.9, 128.8, 130.3, 132.0, 132.1, 135.7, 137.6, 142.2, 142.3 ppm. MS: *m*/*z* (%) = 530 $[M + 4]^+$, 528 $[M + 2]^+$, 526 (37) $[M]^+$, 491 (100), 455 (68), 353 (29), 228 (17), 130 (9), 102 (15). $C_{32}H_{16}Cl_2N_4$ (527.40): calcd. C 72.87, H 3.06, N 10.62; found C 72.95, H 2.98, N 10.70.

(*E*,*E*)-1,4-Dichloro-1,2,3,4-tetrakis(4-nitrophenyl)buta-1,3-diene (5c): This compound was obtained by the oxidation of diarylacetylene **1c** (200 mg, 0.75 mmol) with PbO_2 (180 mg, 0.75 mmol) in HSO_3F (5 mL) at –50 °C in 2 h. Yield 143 mg (63%). M.p. 257–260 °C (decomp.). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 7.30 (d, *J* = 8.9 Hz, 4 H, Ar), 7.64 (d, *J* = 8.8 Hz, 4 H, Ar), 8.07 (d, *J* = 8.9 Hz, 4 H, Ar), 8.15 (d, *J* = 8.8 Hz, 4 H, Ar) ppm. MS: *m*/*z* (%) = 610 $[M + 4]^+$, 608 $[M + 2]^+$, 606 (28) $[M]^+$, 571 (57), 525 (100), 358 (39). $C_{28}H_{16}Cl_2N_4O_8$ (607.35): calcd. C 55.37, H 2.66, N 9.22; found C 55.43, H 2.70, N 9.25.

(*E*,*E*)-1,4-Dichloro-1,2,3,4-tetrakis(3-nitrophenyl)buta-1,3-diene (5d): This compound was obtained by the oxidation of diarylacetylene **1d** (200 mg, 0.75 mmol) with PbO_2 (180 mg, 0.75 mmol) in HSO_3F (5 mL) at –75 °C in 2 h. Yield 152 mg (67%). M.p. 292–294 °C. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 7.63–7.68 (m, 4 H, Ar), 7.89–7.91 (m, 4 H, Ar), 8.06–8.18 (m, 6 H, Ar), 8.37 (t, *J* = 2.0 Hz, 2 H, Ar) ppm. MS: *m*/*z* (%) = 610 $[M + 4]^+$, 608 $[M + 2]^+$, 606 (100) $[M]^+$, 571 (74), 525 (69), 429 (20), 350 (34), 337 (26), 169 (29), 150 (30). $C_{28}H_{16}Cl_2N_4O_8$ (607.35): calcd. C 55.37, H 2.66, N 9.22; found C 55.35, H 2.70, N 9.23.

Conversion of Butadienes 5a–c into Naphthalenes 6a–c: Compounds **5a**–**c** underwent spontaneous transformation into naphthalenes **6a**–**c** on keeping in the air at room temperature over ca. 1–2 months (30–60 d). Compounds **6a**–**c** were purified by recrystallisation.

6-Acetyl-2,3,4-tris(4-acetylphenyl)-1-chloronaphthalene (6a): This compound was obtained from butadiene **5a** (100 mg) in 60 d. Yield 30 mg (32%). Characteristics and X-ray analysis data were published previously.[9]

1-Chloro-6-cyano-2,3,4-tris(4-cyanophenyl)naphthalene (6b): This compound was obtained from butadiene **5b** (100 mg) in 60 d. Yield 49 mg (53%). Recrystallised from ethanol. M.p. 230–233 °C (decomp.). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 6.86 (d, *J* = 8.2 Hz, 2 H, Ar), 7.19 (d, *J* = 8.3 Hz, 2 H, Ar), 7.21 (d, *J* = 8.6 Hz, 2 H, Ar), 7.27 (d, *J* = 8.6 Hz, 2 H, Ar), 7.55 (d, *J* = 8.2 Hz, 2 H, Ar), 7.62 (d, *J* = 8.3 Hz, 2 H, Ar), 7.82 (d, *J* = 1.5 Hz, 1 H, Ar), 7.87 (dd, *J* = 8.8, 1.5 Hz, 1 H, Ar), 8.61 (d, *J* = 8.8 Hz, 1 H, Ar) ppm. MS: *m*/*z* (%) = 492 $[M + 2]^+$, 490 (100) $[M]^+$, 455 (26). $C_{32}H_{15}ClN_4$ (490.94): calcd. C 78.29, H 3.08, N 11.41; found C 78.30, H 3.05, N 11.39.

1-Chloro-6-nitro-2,3,4-tris(4-nitrophenyl)naphthalene (6c): This compound was obtained from butadiene **5c** (100 mg) in 30 d. Yield 51 mg (45%). Recrystallised from acetone. M.p. >330 °C. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 7.44 (d, *J* = 8.6 Hz, 2 H, Ar), 7.61 (d, *J* = 8.5 Hz, 2 H, Ar), 7.67 (d, *J* = 8.4 Hz, 2 H, Ar), 7.88 (d, *J* = 8.4 Hz, 2 H, Ar), 8.17 (d, *J* = 8.5 Hz, 2 H, Ar), 8.23 (d, *J* = 8.6 Hz, 2 H, Ar), 8.42 (d, *J* = 2.2 Hz, 1 H, Ar), 8.56 (dd, *J* = 9.3,

2.2 Hz, 1 H, Ar), 8.78 (d, J = 9.3 Hz, 1 H, Ar) ppm. MS: m/z (%) = 572 $[M + 2]^+$, 570 (100) $[M]^+$, 540 (20), 350 (24), 337 (20), 174 (18). $C_{28}H_{15}ClN_4O_8$ (570.89): calcd. C 58.91, H 2.65, N 9.81; found C 58.94, H 2.65, N 9.80.

Oxidation of Diarylacetylene 1c in the HSO_3F/PbO_2 System with Subsequent Reaction Quenching with Hydrobromic Acid: Diarylacetylene **1c** (200 mg, 0.75 mmol) was dissolved in HSO_3F (5 mL) at –50 °C (dry ice/acetone bath), and PbO_2 (180 mg, 0.75 mmol) was then added with vigorous magnetic stirring. After stirring at this temperature during 2 h, the reaction mixture was quenched with cooled concentrated hydrobromic acid (≈50 mL) at –60 °C. The mixture was diluted with water, and allowed to warm to room temperature. The solid residue was filtered off, washed with water, and dried in air. Column chromatography separation of products **9** and **10** failed. Spectral characteristics of the individual compounds **9** and **10** were obtained from the spectra of the mixture.

(*E*,*E*)-1,4-Dibromo-1,2,3,4-tetrakis(4-nitrophenyl)buta-1,3-diene (9): Yield 50 mg (19%). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 7.33 (d, J = 9.0 Hz, 4 H, Ar), 7.61 (d, J = 9.0 Hz, 4 H, Ar), 8.07 (d, J = 9.0 Hz, 4 H, Ar), 8.11 (d, J = 9.0 Hz, 4 H, Ar) ppm. MS: m/z = 698 $[M + 4]^+$, 696 $[M + 2]^+$, 694 $[M]^+$.

1-Bromo-6-nitro-2,3,4-tris(4-nitrophenyl)naphthalene (10): Yield 90 mg (39%). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 7.29 (d, J = 8.0 Hz, 2 H, Ar), 7.31 (d, J = 9.0 Hz, 2 H, Ar), 7.52 (d, J = 9.0 Hz, 2 H, Ar), 7.97 (d, J = 8.0 Hz, 2 H, Ar), 8.20 (d, J = 9.0 Hz, 2 H, Ar), 8.21 (d, J = 1.5 Hz, 1 H, Ar), 8.22 (d, J = 9.0 Hz, 2 H, Ar), 8.27 (dd, J = 9.0, 1.5 Hz, 1 H, Ar), 8.78 (d, J = 9.0 Hz, 1 H, Ar) ppm. MS: m/z = 616 $[M + 2]^+$, 614 (100) $[M]^+$.

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