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Surface-Modified Carbon Felts: Possible Supports for Combinatorial Chemistry

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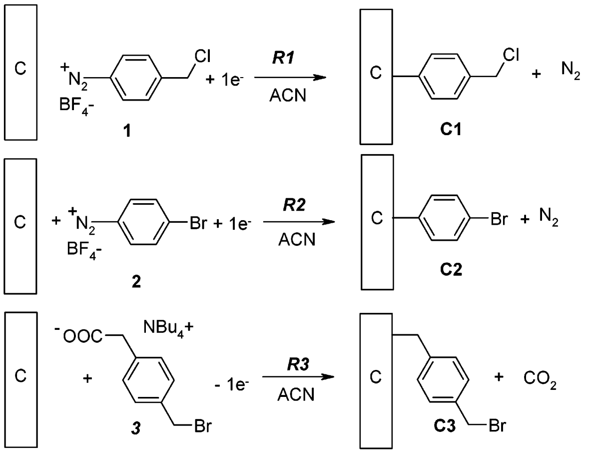
It is possible to prepare carbon-based analogues of the Merrifield resin by electrochemical reduction of diazonium salts or oxidation of aryl acetates on high specific surface area carbon felts. These modified felts can undergo further reactions: nucleophilic substitution, Suzuki reaction, and finally reductive electrochemical cleavage, taking advantage of the conductivity of the carbon felt. This provides a simple example of the possible use of electrochemistry in combinatorial synthesis.

Introduction

We have shown recently that it is possible to prepare carbon materials with high specific surface area and well-defined functionalities covalently attached to the surface.[1] This was achieved by electrochemical reduction of diazonium salts[2] or oxidation of aryl acetates[3] using a carbon felt with a high specific surface area (Actitex 1500-1, 1500 $m^2\ g^{-1}$) as the working electrode. Three different surface-modified felts were prepared; they are shown in Scheme 1. The organic groups present on the surface were characterized by elemental analysis, by X-ray photoelectron spectroscopy (XPS), by scanning microscopy/energy dispersive X-ray spectrometry (EDS), and by IR spectroscopy. It was also possible to measure the capacity of these materials, 1.73, 0.88, and 1.83 mmol g^{-1}, and the surface concentrations (calculated on the basis of 1500 $m^2\ g^{-1}$ for the specific surface of the carbon felt), 1.47, 0.70, and 1.71×10^{-10} mol cm^{-2}, for **C1**, **C2**, and **C3**, respectively. These capacities can be favorably compared to those of commercial resins for ion exchange or for combinatorial chemistry; this is due to the very large specific surface area of the felt. The attachment of the organic groups to the surface is strong as these groups cannot be removed by prolonged rinsing in an ultrasonic cleaner in various organic solvents.[1−3]

These materials can find a large variety of applications including ion exchange materials, catalysts, or supports for combinatorial chemistry. As concerns this last application, the carbon support is robust and insensitive to the solvent and there is no swelling problem as with styrene−divinylbenzene resins. Besides, the conductivity of the carbon makes possible the inclusion of electrochemical steps (including the cleavage step) in the combinatorial synthesis. In this paper we report a simple sequence to demonstrate the possibility of solid-phase chemistry on this carbon material including an electrochemical cleavage step. Preceding investigations dealing with combinatorial chemistry including electrochemical steps have been published by J. Simonet and co-workers;[4] they made use of a polythiophene matrix electropolymerized on a platinum electrode. The polythiophene was substituted in the 3-position by a linker and the reactive SO_2Cl function. Cleavage of the amine previously attached to the SO_2Cl group was achieved by electrochemi-

SCHEME 1



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cal cleavage of the S−N bond. An electrochemical setup specially designed for parallel electrosynthesis (spatially addressable electrolysis platform) has been devised by Yudin and co-workers.[5] It was used for the anodic oxidation of carbamates, amides, and sulfonamides, which led to libraries of α-alkoxycarbamates, α-alkoxyamides, and α-alkoxysulfonamides.[5] Similarly, the intramolecular cyclization of hydroxamides provided heterobicyclic compounds in high yields, and hydrocoupling of aldimines yielded vicinal diamines. The instrumentation for parallel electrochemical synthesis has been described.[5a]

Results and Discussion

Among the three carbon materials of Scheme 1 we choose **C1** and **C3** for further studies as these materials are analogues of a Merrifield resin and substitution of the halogen should be easy, much easier than the substitution of the bromine of **C2**. The modified carbon felts **C1** and **C3** were prepared[1] in the form of disks (22 mm diameter, 2 mm thick) in the following way: the 4-chloro- or bromomethylphenyl group was attached to the carbon felt by electrochemical reduction of the tetrafluoroborate of 4-chloromethylbenzenediazonium or by electrochemical oxidation of 4-bromophenylacetate tetramethylammonium. This was achieved in a circulating cell[6] where the solution (ACN + 0.1 M NBu_4BF_4 + substrate) flows through carbon felt disks packed in the working compartment. Two counter electrodes are separated from the working compartment by ion exchange membranes. As the solution flows through the carbon felt disks, the disk close to the inlet will be termed upstream and that close to the outlet downstream. The potential of the carbon felt is maintained by a potentiostat (see the Experimental Section). After completion of the electrolysis, the carbon felt disks were thoroughly rinsed ultrasonically in different solvents and then dried. Characterization of the modified carbon felts[1] was achieved by elemental analysis, XPS, scanning electron microscopy/EDS, and IR spectroscopy.

The reaction sequence of Scheme 2 was then attempted. The benzylic chlorine or bromine was first substituted by an aromatic thiolate to give a sulfide. Using differently 4-X substituted thiolates, we could obtain **C4** (X = F), **C5** (X = Cl), **C6** (X = Br), **C7** (X = CF_3), and **C8** (X = NO_2). Starting from **C5** (n =0) and **C6** (n=0), which are substituted by a chlorine or bromine, respectively, it was then possible to perform a Suzuki reaction to obtain **C9** (Y = CF_3) and **C10** (Y = H). Electrochemical cleavage of the benzylic carbon−sulfide bond is then possible due to the conductivity of the carbon, and **4** was obtained by reduction of **C10**.

The nucleophilic substitution of **C1** was achieved by placing the disks at reflux either in a round-bottom flask or in a Quest Argonaut reactor. The results of these experiments are reported in Table 1.

SCHEME 2

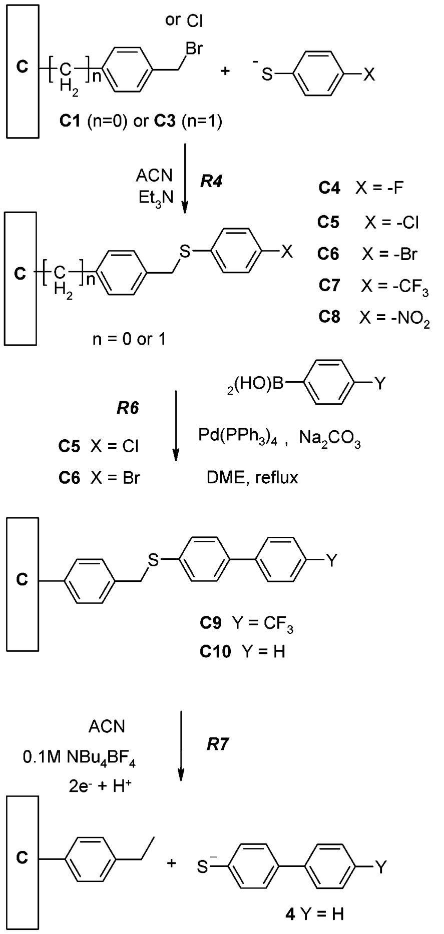

TABLE 1. Yields of Nucleophilic Substitution Reaction R4[a]

starting and obtained material	X (amt of thiol (equiv))	amt of NEt_3 (equiv)	conditions[b]	yield[c] (%)	ratio X/S[a]
C1 → **C4** (n = 0)	F (15)	20	A, 80 °C, 6 h	44[d]	1
C1 → **C5** (n = 0)	Cl (15)	20	A, 80 °C, 10 h	84	*e*
C1 → **C6** (n = 0)	Br (16)	20	B, 80 °C, 88 h	100	1
C1 → **C7** (n = 0)	CF_3 (15)	20	A, 80 °C, 4 h	13[d]	3
C1 → **C8** (n = 0)	NO_2 (15)	20	A, 80 °C, 10 h	84	*f*
C3 → **C4** (n = 1)	F (41)	41	B, 80 °C, 108 h	24[d]	1
C3 → **C5** (n = 1)	Cl (15)	36	B, 80 °C, 96 h	63	*e*
C3 → **C6** (n = 1)	Br (13)	43	B, 80 °C, 108 h	43	1
C3 → **C7** (n = 1)	CF_3 (31)	41	B, 80 °C, 108 h	43[d]	3
C3 → **C8** (n = 1)	NO_2 (15)	20	A, 80 °C, 10 h	30	*f*

[a] Determined from the elemental analysis. [b] A = Quest Argonaut reactor. B = round-bottom flask with magnetic stirring. [c] Determined from the %S obtained by elemental analysis. [d] Taking into account the 2% F observed in the untreated felt. [e] An excess of chlorine was observed, probably coming from $CHCl_3$ used for rinsing and incompletely eliminated. [f] The felt already contains about 2% N.

The occurrence of the nucleophilic substitution was ascertained by elemental analysis through the determination of sulfur in all experiments and of F (**C4** and **C7**), Cl (**C5**), and Br (**C6**), (see the Experimental Section). The yields are satisfactory to good, but the surface reactions are much slower than in solution, as usually observed. Provided the reaction times are long enough, the yields do not depend very much on the way in which the experiments are performed either simply in a flask or in

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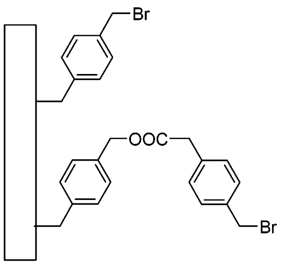
SCHEME 3



a reactor specially designed for combinatorial chemistry. The ratios X/S are in good agreement with the formula of the material, provided that great care is exercised to achieve complete rinsing of the felt to be certain that no supporting electrolytes remain adsorbed. Chloroform is a good rinsing solvent, but further rinsing with ether is necessary. If further rinsing is not done, some chlorine may remain attached to the surface as with **C5**, where the measured chlorine was higher than expected. Starting from **C3** (n =1), the analysis shows that the amount of bromine which has reacted is much higher than the yield of substituted material; for example, in the reaction **C3** → **C8**, 95% of the initial bromine has been consumed but the yield is only 30%. This is likely due to the solvolysis of the bromine by triethylamine. Analysis of the solution after derivatization of the felt by oxidation of 4-bromomethylphenylacetate tetramethylammonium (**C3** obtained through reaction R3) showed the presence of cyclic dimers and trimers stemming from the nucleophilic reaction of the carboxylate on the benzylic bromine. As such reactions could also take place on the surface to give chemically inhomogeneous surfaces as shown in Scheme 3, we discontinued the use of these processes to derivatize the felts.

The substituted felts prepared by reduction of the diazonium salt and nucleophilic substitution by thiolates were further characterized by FTIR spectroscopy and by scanning microscopy/energy dispersive X-ray spectrometry. The FTIR spectrum of the untreated Actitex 1500-1 carbon felt is shown in Figure S1 in the Supporting Information; it shows three large IR bands around 3440, 1970, 1170 cm^{-1}. Figure S2 in the Supporting Information shows the spectrum of **C2** after modification of the same felt by 4-bromophenyl groups. The FTIR spectra of the different materials are reported in Table 2, and the spectrum of **C6** (n = 0) is shown in Figure 1. The spectra of **C4**−**C8** are shown, respectively, in Figures S3−S6 in the Supporting Information. These spectra permit the presence of both the substituents and the aromatic rings to be observed.

The scanning microscopy images permit observation that the fibers of the modified felts[1] are similar to those of untreated felts, indicating that they are not damaged during the chemical reaction and that no thick polymeric layer is formed on the surface. The EDS spectra permit characterization of the substituents as shown in Table 3. In all these spectra one can observe the presence of sulfur (albeit in variable amounts from material to material) as well as that of chlorine as the yields are not quantitative except in the case of **C6**; one also observes the unreacted halogen substituents.

The next step is the reaction of **C5** and **C6** (n = 0) with phenylboronic acid and its 4-fluoromethyl derivative along a Suzuki reaction (**R6**, Scheme 2) to give **C9** and **C10**. The results concerning **C9** are reported in Table 4.

TABLE 2. FTIR Spectra of Modified Carbon Felt

material	wavelength (cm^{-1})	assignment
C4, $n = 0$	1586	ν C=C of aromatic ring
	1487, 1227	F-substituted aromatic ring
	1154−1012	para-F-substituted aromatic ring
	827	para-disubstituted aromatic ring
C5, $n = 0$	1473, 1009	para-Cl-disubstituted aromatic ring
	1092	Cl-substituted aromatic ring
	811	para-disubstituted aromatic ring
	485	para-Cl-substituted aromatic ring
C6, $n = 0$	1469, 1005	para-Br-substituted aromatic ring
	1090, 1066	δ CH of aromatic rings
	807	para-disubstituted aromatic ring
	477	para-Br-substituted aromatic ring
C7, $n = 0$	1395	para-disusbstituted aromatic ring with a CF$_3$
	1322, 1165, 1126	CF$_3$
	1061, 1011	para-CF$_3$-substituted aromatic ring
	823	para-disubstituted aromatic ring
	493	para-CF$_3$-substituted aromatic ring
C8, $n = 0$	1574	para-NO$_2$-substituted aromatic ring
	1510, 1534	NO$_2$
	1182	δ CH of aromatic rings
	851, 838	para-disubstituted aromatic ring
	469	para-disusbstituted aromatic ring with a NO$_2$

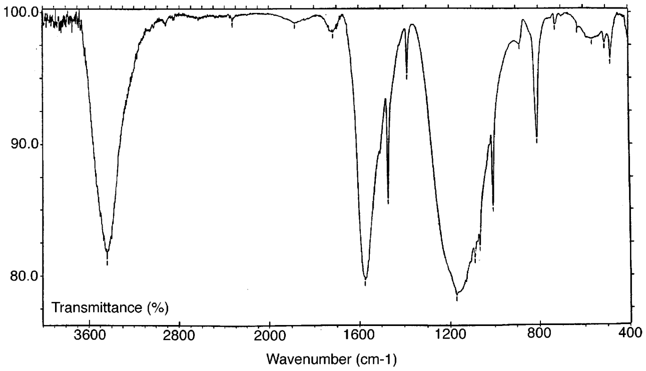


FIGURE 1. FTIR spectrum of **C6**.

TABLE 3. Scanning Microscopy/EDS Spectra[a]

material	analysis (mass %)
C4	C, 75.0; O, 12.1; Cl, 0.9; S, 0.7; F, 0.4
C5	C, 72.1; O, 13.7; S, 4.1; Cl, 5
C6	C, 75.8; O, 14.5; Cl, nd; S, 4.3; Br, 12.8
C7	C, 76.8; O, 8.7; Cl, 2.5; S, 1.0; F, 0.8
C8	C, 77.0; O, 8.6; Cl, 4.1; S, 8.3

[a] Other minor elements are detected: P, Na, Ca, Mg, P.

The occurrence of the Suzuki reaction was ascertained in the case of **C9** by (i) elemental analysis through the increase of the amount of fluorine from 0.2% (as in untreated felts) to 1.89% (starting from **C5**, n = 0) and 1.68% (from **C6**, n = 0) and (ii) FTIR as shown in Table 5 and Figure S6. In the case of **C10** (n = 0) as there is no characteristic substituent we used it directly in the next step.

The above results indicate that the Suzuki reaction is indeed possible but that the yields are low.

As the carbon felts are electronic conductors, it should be possible to cleave electrochemically the molecules

TABLE 4. Formation of C9 from C5 and C6 through a Suzuki Reaction

starting and substituted material	amt of catalyst $Pd(PPh_3)_4$ (equiv)	amt of base Na_2CO_3 (equiv)	boronic acid (amt (equiv))	time (h)	yield (%)
C5 → **C9** (n = 0)	1.9	95	trifluoromethyl (76)	96	32
C6 → **C9** (n = 0)	1.1	55	trifluoromethyl (44)	72	23

TABLE 5. FTIR Spectra of C9

wavelength (cm^{-1})	assignment
1475	para-disubstituted aromatic ring
1385	CF_3
816	para-disubstituted aromatic ring

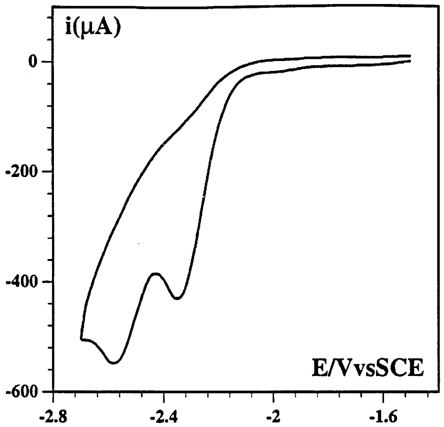


FIGURE 2. Cyclic voltamogram of **5** (c = 2 mM) in ACN + 0.1 M NBu_4BF_4 on a glassy carbon electrode. Reference SCE. Scan rate v = 0.2 V/s.

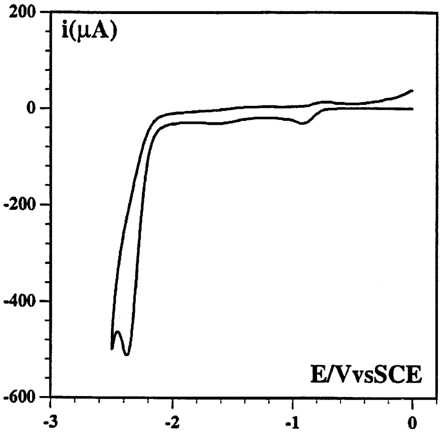
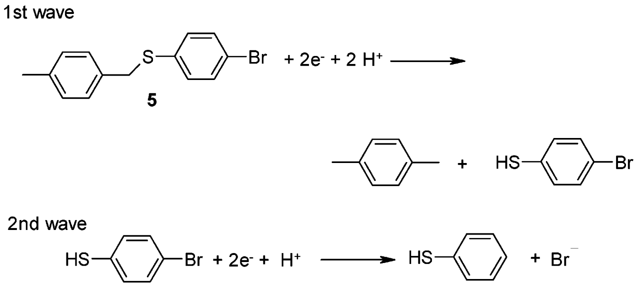


FIGURE 3. Cyclic voltamogram (first wave and reversible thiolate/disulfide system) of **5** (c = 2 mM) in ACN + 0.1 M NBu_4BF_4 on a glassy carbon electrode. Reference SCE. Scan rate v = 0.2 V/s.

SCHEME 4



attached to the surface. We attempted the cleavage of **C6** (X = Br), **C9** (Y = CF_3), and **C10** (Y = H). The cleavage of carbon−sulfur bonds has been previously investigated.[7,8] Upon electrochemical reduction, C_6H_5SR sulfides (R = CH_3, C_2H_5, *i*-Pr, *t*-Bu) are cleaved at about −2.7 V/SCE to give $C_6H_5S^-$ and RH.[9] To determine the cleavage potential of **C6**, we synthesized 4-methylbenzyl 4′-bromophenyl sulfide (**5**). Its cyclic voltammetry (on glassy carbon in ACN + 0. 1 M NBu_4BF_4) presents two irreversible cathodic waves at $E_{p_1} = -2.36$ V/SCE (which remains irreversible up to 200 V s^{-1}) and $E_{p_2} = -2.58$ V/SCE (Figure 2). The first one is assigned to the cleavage of the carbon−sulfur bond and the second one to the cleavage of the C−Br bond (Scheme 4). If the cathodic potential scan is limited to −2.50 V/SCE, one can observe a reversible system at $E° = -0.78$ V/SCE which corresponds to the couple thiolate/diphenyl disulfide ($BrC_6H_4S^-$/$[BrC_6H_4S]_2$) (Figure 3). The cleavage of the benzylic carbon−sulfur bond of **C6** was then accomplished in a circulation cell[6] in ACN + 0.1 M NBu_4BF_4 at a potential of −2.3 V/SCE for 1 h. Analysis of the felt after electrolysis indicated a decrease of the %S from 5.65% to 0.77% and of Br from 15.25% to 3.49%, from which a yield of 86% could be calculated.

Analysis of the electrolysis solution after extraction with ethyl acetate indicated the presence of $BrC_6H_4SSC_6H_4Br$ (**6**) obtained by oxidation of the thiolate during the workup. Minor products were also detected, resulting from the cleavage of the C−Br bond. If the extraction is performed with CH_2Cl_2, a 17% yield of $BrC_6H_4SCH_2SC_6H_4Br$ (**7**) is obtained, resulting from the attack of the thiolate on dichloromethane and giving additional evidence of the formation of the thiolate and the occurrence of the cleavage reaction.

To determine the reduction potential of **C9** and **C10**, we synthesized 4-methylbenzyl 4′-trifluoromethylbiphenyl sulfide (**8**) and 4-methylbenzyl biphenyl sulfide (**9**). The cyclic voltammetry of **8** presents first a $2e^-$ irreversible reduction wave located at $E_{p_1} = 2.05$ V/SCE corresponding to the cleavage of the benzylic carbon−sulfur bond (Figure 4). The second $6e^-$ irreversible reduction wave at $E_{p_2} = -2.42$ V/SCE corresponds to the stepwise cleavage of the CF bonds (Scheme 5).[10] On the basis of these results, we attempted the cleavage of the C−S bond of **C9** at a potential of −2.0 V/SCE for 6 h. Analysis of the felt showed that the %S and %F decreased to negligible values, but analysis of the resulting solution

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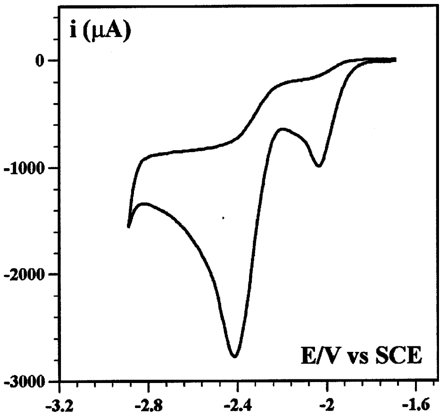
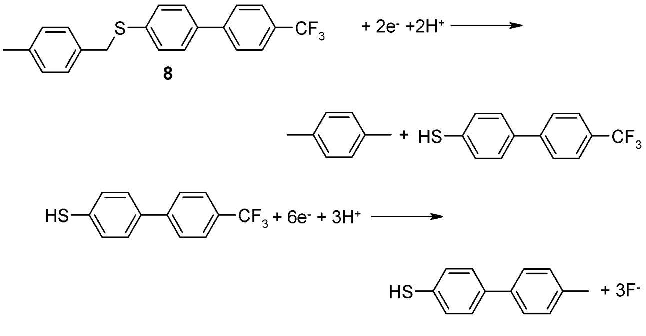


FIGURE 4. Cyclic voltamogram of **8** ($c = 1.27$ mM) in ACN + 0.1 M NBu_4BF_4 on a glassy carbon electrode. Reference SCE. Scan rate $v = 0.2$ V/s.

SCHEME 5



showed that it consisted of a complex mixture likely stemming from the cleavage of the C−F bonds. This is likely due to an unproper control of the potential inside the felt (see the Experimental Section, Circulation Cell). We then investigated the cyclic voltammetry of **9** as a model of **C10**. It presents a $2e^-$ irreversible cathodic wave at $E_p = -2.23$ V/SCE, and on the anodic return scan the oxidation wave of biphenyl thiolate is observed at $E_{p_{an}} = -0.12$ V/SCE. **9** was electrolyzed at −2.2 V/SCE, and biphenylthiol (**4**, Y = H) was identified by comparison with an authentic sample.[11] In the same way, **C10** was electrolyzed at −2.2 V/SCE in a circulating cell,[6] and the resulting solution was shown to contain biphenylthiol identical with the reduction product of **9** and with an authentic sample. Thiphenylphosphine which had been retained in the felt despite vigorous rinsing and triethylamine coming from the supporting electrolyte were detected as impurities.

Conclusion

We have shown previously that analogues of Merrifield resins could be prepared on carbon felts and that the loading of these felts was equivalent to that of commercial resins. We have now shown that these modified felts could be used for solid-phase synthesis. Many other reactions besides those described in this paper could be used, and they should permit inclusion of electrochemical steps in the synthesis. For example, as suggested by a reviewer, **C2** could be substituted by suitably chosen nucleophiles such as thiolates via an $S_{RN}1$ reaction; oxidation by H_2O_2 into sulfones and then electrochemical cleavage into sulfinates (easily converted to sulfonyl chlorides) would open the way to easy and very versatile supported synthesis using a very convenient and cheap substrate. Among the large number of organic electrochemical reactions which have been investigated up to now, one can find many more examples of electrochemical cleavage[7] reactions which could be useful for combinatorial synthesis: (i) Carbon−carbon bonds in pinacols, diketones, and chalcones can be cleaved by reduction or oxidation. (ii) Carbon−oxygen bonds can be cleaved by reduction of esters of aromatic acids and alcohols. Acyl derivatives of phenols can be cleaved to phenolate and acyl radical. Carbonyls conjugated with aromatic systems cleave rapidly such as in benzyl benzoate, which cleaves rapidly to benzoate and benzyl radical, which leads to toluene. (iii) Besides thioethers described in this paper, sulfonium ions, sulfoxides, thioesters, and sulfones can be cleaved upon electrochemical reduction.[8] (iv) Carbon−nitrogen bonds can be cleaved upon electrochemical reduction in quaternary ammoniums and in benzamides,[12] which give good yields of benzylamines upon electrochemical reduction. But the use of electrochemistry in combinatorial synthesis could be expanded beyond cleavage steps to modification of attached groups by reduction or oxidation and to coupling reactions, for example, the coupling of activated alkenes,[13] one of the alkenes already being attached to the support and the other one being in solution. One can also think of oxidative couplings[14] such as with aryl ethers or amines or to the Kolbe reaction. It should therefore be possible to use already known reactions in a new context to provide new and hopefully interesting compounds. However, the failure to prepare the trifluoromethylbiphenylthiol by reduction of **C9** indicates that some improvements should be made in the design of the cell to control as perfectly as possible the potential inside the whole volume of the felt.

Experimental Section

Carbon Felt. All the experiments were made with Actitex 1500-1 with a specific surface area of 1500 $m^2\ g^{-1}$. Typical analysis (undegassed): C, 79.53; H, 0.64; N, 0.98; O, 3.04; S, ϵ; I, ϵ; Cl, ϵ; Br, ϵ; F, 0.20 (ϵ = not quantifiable). The FTIR spectrum of the felt shows two large absorption bands at 1560 and 1140 cm^{-1} which correspond to the vibrations of the carbon skeleton. The EDS spectrum shows the following: C, 87.0; O, 10.6; Cl, 0.2; P, 1.5; Na: 0.1. Disks with 22 mm diameter were cut into 2 mm thick sheets of the felt.

Circulation Cell.[6] All the derivatizations of the felts as well as the further electrochemical cleavage reaction were

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performed in a circulating cell analogous to that described by Moinet.[6] The cell is made of Teflon and glass assembled as in filter press cells. The working electrode is made from eight carbon felt disks pressed together inside a Teflon cylinder. The contact to the carbon felt disks is made with graphite paper. There are two carbon counter electrodes separated from the working electrode by ion exchange membranes. The reference electrode is a Ag/AgCl electrode inserted close to the working electrode through a hole in the Teflon cylinder. The flow of electrolyte and substrate is pumped by a peristaltic pump through the felt in the Teflon cylinder, which constitutes the compartment of the working electrode. A potentiostat maintains the potential of one of the counter electrodes (current I_1 flows through this electrode) to obtain the desired potential difference between the working and the reference electrodes; the current of the second counter electrode (I_2) is maintained by a galvanostat under automatic control by I_1 so that $I_1/I_2 = 1.9$, where I_1 and I_2 are the currents flowing to or from the upstream or downstream counter electrode, respectively.[6] At the end of the electrolysis the disks were rinsed for 5 min in each of the solvents acetonitrile, chloroform, acetone, and diethyl ether and dried for 24 h in an oven at 40 °C.

During the electrolysis of **C9** it has been shown above that the C−S bond is cleaved but that C−F bonds are also cleaved although the peak potential corresponding to this process is about 0.4 V more negative. It therefore seems that at least some parts of the felts must reach more negative potentials than that imposed by the potentiostat. With the complex structure of such felts including meso- and micropores, it is likely that the felt is not entirely equipotential and that ohmic drop should lower the potential, not increase it. Further studies should be carried out to solve this problem.

Cyclic voltammetry was performed in ACN + 0.1 M NBu_4BF_4 as supporting electrolyte on 3 mm diameter carbon disk electrodes previously polished with 1 μm diamond paste and ultrasonically rinsed in ACN.

Characterization of the Felts.

Elemental analyses where made at CRVA (Aventis, Vitry, France) with undegassed felts, which explains that the sum of the elements does not amount to 100%.

Scanning Electronic Microscopy/EDS. The mass percent of the elements is normalized to 100%.

Modification of the Carbon Felts. C1 was prepared by electrolysis of a 5×10^{-3} M solution of $^{-}BF_4{}^{+}N_2C_6H_4CH_2Cl$ at −0.8 V SCE for 2 h and then rinsed in an ultrasonic cleaner for 5 min in each of the solvents acetonitrile, chloroform, acetone, and ether and dried for 24 h in an oven at 40 °C. Elemental analysis: C, 77.30; H, 2.07; N, 2.05; Cl, 6.13; F, 0.44. The XPS spectrum shows the doublet of $Cl_{2p_{3/2}}$ and $Cl_{2p_{1/2}}$: 1.7%. The EDS spectrum shows the following: C, 87.0; O, 11.3; Cl, 0.5; P,1.1; Ca, 0.1; S, 0.1. FTIR spectrum (cm^{-1}): 2923 (ν_a CH_2 alkyl), 2853 (ν_s CH_2 alkyl), 1503 (ν C=C aromatic rings), 1016−1084 (δ CH aromatic rings), 808 (para-disubstituted aromatic rings).

C3 was prepared by electrolysis of a 1.4×10^{-2} M solution of $^{+}Me_4N^{-}BrCH_2C_6H_4$ in ACN + 0.1 M NBu_4BF_4 at +1.2 V/SCE for 2 h and then rinsed and dried as above. Elemental analysis: C, 76.49; H, 1.00; N, 1.46; O, 6.25; Br, 6.32. The XPS spectrum shows the doublet of $Br_{3d_{5/2}}$ and $Br_{3d_{3/2}}$ at 71 and 72 eV: 0.45%. The EDS spectrum shows the following: C, 82.3; O 14.1; Cl, 0.5; Br, 1.4; P, 1.0.

Elemental Analysis. C4: C, 74.26; H, 1.41; N, 2.04; F, 1.18; Cl, 9.06; S, 1.96. **C5:** C,78.39; H, 1.20; N,1.69; Cl, 9.14; S, 3.78; O, 4.50. **C6**: C, 66.44; H, 1.50; N, 0.33; Br, 14.25; S, 5.65. **C7**: C, 78.81; H, 1.57; N, 1.93; F, 1.10; Cl, 3.36; S, 0.60. **C8**: C, 74.57; H, 1.60; N, 3.07; O, 8.15; S, 3.76; Cl, 5.30. **C9** (obtained from **C5**): C, 78.42; H, 1.90; N, 1.06; S, 1.85; F, 1.89; Cl, 2.96. **C9** (obtained from **C6**): C, 65.70; H, 1.80; N, 1.40; S, 0.18; F; 1.68; Cl, 2.26. **C10**: C, 78.66; H, 1.63; N, 1.84; S, 1.73.

The loadings of the felts were calculated as in commercial resins: for example, with $-C_6H_4CH_2Cl$, the %Cl being x, the loading is $10x/35.5$ mol of Cl/g of modified felt.

4-Methylbenzyl 4′-Bromophenyl Sulfide (5). A 1.04 g sample of 4-methylbenzyl bromide (5.52 mM, 1 equiv) and 1.07 g of 4-bromobenzenethiol (5.66 mM, 1 equiv) were dissolved in 60 mL of acetonitrile. A 1 mL sample of triethylamine was then added (7.17 mM, 1.3 equiv), and the solution was refluxed under argon. The reaction was followed by CCM (cyclohexane/ethyl acetate, 6/4). After 1 h of reaction, the thiol had completely reacted. The solvent was evaporated and the resulting product extracted with CH_2Cl_2 in the presence of 1 M HCl. The residue was purified on a silica gel column eluted with cyclohexane to give a white solid (1.37 g, 4.68 mM, yield 83%). Mp: 90 °C. Anal. Calcd for $C_{14}H_{13}BrS$: C, 57.33; H, 4.43; S, 10.92; Br, 27.30. Found: C, 57.48; H, 4.51; 11.06; Br, 27.06. ^{1}H NMR (DMSO-d_6): δ (ppm) 2.33 (s, 3H, CH_3), 4.07 (s, 2H, CH_2), 7.00−7.37 (m, 8H, aromatics). MS (EI, 70 eV): m/z = 294 (MH^+), 187 ($SC_6H_4Br^+$), 105 ($CH_3PhCH_2{}^+$).

4-Methylbenzyl 4′-Trifluoromethylbiphenyl Sulfide (8). 8 was prepared as **9** below. White solid (yield 62%). Anal. Calcd for $C_{21}H_{17}SF_3$: C, 70.39; H, 4.74; S, 9.93. Found: C, 70.68; H, 5.06; S, 10.02. ^{1}H NMR (DMSO-d_6): δ (ppm) 2.34 (s, 3H, CH_3), 4.16 (s, 2H, CH_2), 7.1−7.9 (m, 12H, aromatics). MS (EI, 70 eV): m/z = 358 (MH^+), 253 ($^{+}SC_6H_4C_6H_4{-}CF_3$), 105 ($CH_3PhCH_2{}^+$).

4-Methylbenzyl 4′-Biphenyl Sulfide (9). A 0.40 g sample of 4-methylbenzyl 4′-bromophenyl sulfide (1.37 mM, 1 equiv) was stirred under argon in the presence of tetrakis(triphenylphosphine)palladium (0.14 mM, 0.1 equiv) in 20 mL of DME for 5 min at room temperature. Phenylboronic acid (0.34 g, 2.74 mM, 2.0 equiv) and 2.4 mL of a 2 M aqueous solution of Na_2CO_3 (4.8 mM, 3.5 equiv) were then added to the orange solution. The reaction medium was refluxed, and the solution became brown and then black. The reaction was followed by CCM (cyclohexane/dichloromethane, 8/2). After 6 h, heating was discontinued and the solvent evaporated. The brown residue was purified on a silica gel column (cyclohexane/dichloromethane, 8/2) to give 0.28 g (0.96 mM, 71% yield) of a white solid. Mp: 116 °C. Anal. Calcd for $C_{20}H_{18}S$: C, 82.75; H, 6.20; S, 11.03. Found: C, 82.31; H, 6.27; S, 10.92. ^{1}H NMR (DMSO-d_6): δ (ppm) 2.26 (s, 3H, CH_3), 4.15 (s, 2H, CH_2), 7.0−7.7 (m, 13H, aromatics). MS (EI, 70 eV): m/z = 290 (MH^+), 184 ($^{+}SC_6H_4C_6H_5 - H$), 152 ($^{+}C_6H_4C_6H_4$), 105 ($CH_3PhCH_2{}^+$).

Biphenylthiol (4)[11] was obtained as described. It was identified with the products obtained by cleavage of either **9** or **C10** by TLC, NMR, and MS (m/z = 186, M^+).

C9 and **C10** were prepared in the same way as **8** and **9**, but after addition of the boronic acid, reflux was maintained for 4 days. The felts were then rinsed in an ultrasonic cleaner successively in water, ethanol, acetone, chloroform, and diethyl ether and dried for 24 h in an oven at 40 °C.

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Supporting Information Available: FTIR spectra of Actitex 1501, **C2**, **C4**, **C5**, and **C7**−**C9**. This material is available free of charge via the Internet at http://pubs.acs.org.

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