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THE CONDUCTIVE SULFUR/CARBON MIXTURE CATHODE.
AN EFFICIENT SYNTHESIS OF THIOPHENES AND RELATED COMPOUNDS FROM ACETYLENES

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The electroreduction of Michael acceptors such as acetylenic derivatives at a compact sulfur-carbon electrode in aprotic media affords thioorganic compounds, mainly thiophenes, in fairly high yields. Their formation is discussed as a function of the electronic effect of the substituents on the acetylenic triple bond.

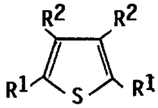
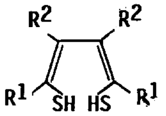
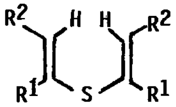
Development of mixed electrolyses[1,2] represents a hopeful future for organic electrochemistry. In most cases, the aim is to produce nucleophiles and bases at the cathode, and electrophiles and acids at the anode. Reagents, present in solution, react with the transient species formed at the electrodes (in general they are chosen to have no electrochemical reactivity towards the working electrode).

More rarely, one of the constituents involved in the mixed electrolysis is incorporated, in the solid state, to the conductive matrix of the working electrode. Thus the electrochemical functionalization of electroactive polymers or graphite would be such a case. One can also dissolve in the conductor (graphite dust or any metal powder or any conducting polymer) some insoluble or weakly soluble electroactive material, the concentration of which does not provoke a marked drop in the conductivity of the system. Examples are the mixtures sulfur/graphite[3] and selenium/graphite,[4] the use of which was recently developed following pioneer work by BERGE[5].

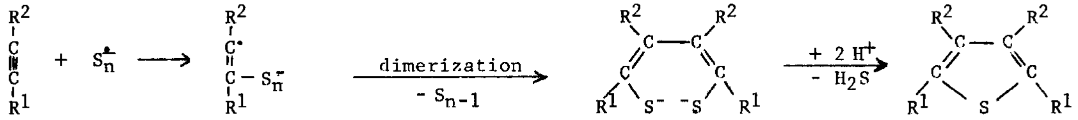
We now report another kind of use of sulfur/carbon electrodes, involving the reduction of Michael acceptors such as acetylenic bonds substituted by at least one strongly withdrawing group. The substrates **1** were tested ; their normal potentials (referenced to a SCE in dry DMF/tetraethylammonium perchlorate 0.1 M - platinum microcathode) are too negative towards the potential applied to the S — C cathode (-0.9 V *vs* SCE) to expect a mixed coupling of reduction products. In the table we gave the yields of isolated products after electrolysis in well defined conditions[6].

Although the reactivity of the species present at the interface before or after the charge(s) transfer has not been clarified so far, the mode of this mixed electrolysis must be expected to obey to complex rules specific of the nature of the cathodic material. We have noted that the reactivity of **1** is strongly increased on the S — C cathode when polarized. Moreover, dianions $S^=$ or $S_n^=$ derived from sulfur react differently on **1** (formation of products of the type **4** exclusively). Consequently, it is possible that the formation of the C — S bond (nucleophilic attack) and the C — C bond (radical coupling) occur more or less simultaneously in conditions which have to be extended to other Michael acceptors.

A preliminary scheme may be proposed for the 1,2-disubstituted acetylenes studied. The mechanism is based on the strong withdrawing effect of groups R^1 or/and R^2 and the nucleophilic character of the transient $S_n^{\bullet -}$ formed in the matrix of the material.

$R^1-C\equiv C-R^2$		1	E_p V (*vs* aq. SCE)	Isolated products		
R^1	R^2			 2	 3	 4
H	Ph	a	- 2,55		no reaction	
H	CO_2Et	b	- 2,0	10		12*
Ph	CHO	c	- 1,50	82		
Ph	CO_2Me	d	- 1,70	85		
Ph	CN	e	- 1,72	80		7
CO_2Me	CO_2Me	f	- 1,30	32	53	

* a sulfur containing trimer is also isolated [6 %] = 1,3,5-tricarboethoxy-2,4,6-trimercaptobenzene.



Shortened chains S_{n-1} may be reduced again (increase of the electrolysis current dependent on the rate addition) and H_2S (or $S^{=}$) may act classically to lead a restricted amount of **4**.

It must be outlined that acetylenes may react with sulfur (obtainment of traces of thiophenes together with other complex heterocycles) in much more drastic conditions [7].

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6. **Electrolysis conditions** . Acetylenic compounds are commercially available from JANSSEN CHIMICA (**1a**) or prepared as described in literature : **1b**[8], **1c**[9], **1d**[10], **1e**[11], **1f**[12].- The working cathode is prepared by plunging a metallic wire into a pasty mixture of 1 part of carbon powder, 2 parts of sulfur heated and melted at 130° C in a test tube. After return to room temperature, the test tube is broken to release the compact electrode [A – 20 cm^2].- Electrolyses are carried out in a three compartment H-cell. Supporting electrolyte : $NaClO_4$ 0.5 M in DMF - substrate concentration : 0.125 M. Working potential : -0.9 V versus SCE.- At the beginning of electrolysis the current intensity is about 200 mA. It decreases to almost zero after an electric consumption of 2 Faradays per mole. At the end of the run, the compact electrode is far from being completely consumed. The carbon powder still in suspension in the reaction mixture is then filtered off, and the DMF distilled under low pressure ; the water washed residue is extracted with ether. Reaction products are isolated after chromatography on a silica-gel column eluted with a suitable solvent, and well characterized by IR spectroscopy, NMR and mass spectroscopy.
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