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Cathodic Cleavage of Carbon - Oxygen Bonds of Ethers. A Selective Monosubstitution of Triphenylene Hexaethers in Electrophilic Media

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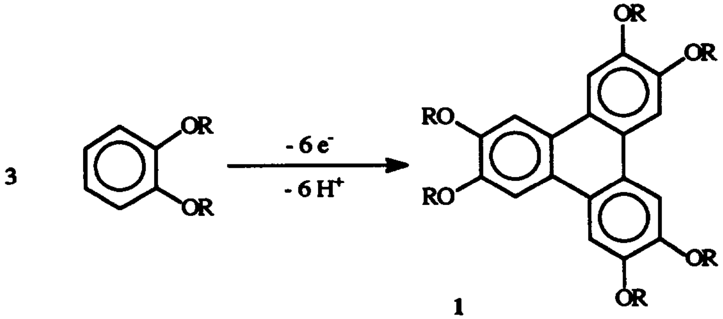
<u>Abstract</u> : The selective cleavage limited to one carbon - oxygen bond for hexaalkoxytriphenylenes can be cathodically performed in aprotic dipolar solvents. The functionalization of the transient phenate by various electrophiles was achieved ex situ after electrolysis completion.

The chemical and electrochemical oxidations of aromatic orthodiethers (now well documented) give rise to the corresponding triphenylenes. This anodic trimerization was shown[1] to be an attractive method for obtaining triphenylenes, especially when the presence of various ether groups is wished as substituents. Moreover, structures **1** are known to behave as redox centers (both formation of cation radicals and anion radicals) and may also be considered[2] according to the nature of OR substituents as discotic materials (when R is a long alkyl or a polyether chain).



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The selective and limited functionalization of compounds **1** is worth performing both to synthesize new discotic structures and introduce specific groups with the aim of grafting specific redox centers or even crown ether moieties (then attached to **1**) to different kinds of polymers or active surfaces. In order to achieve such selective functionalizations with a good selectivity, it is here proposed, since classical methods of reduction of aromatic ethers are far from selective[3], to use the method relative to the cathodic scission of aromatic ethers already reported[4] and detailed in the case of monoethers. In general, the two-electron cleavage appears to obey the scheme below and the electrochemical potential necessary for the first reaction to take place depends on the level of the LUMO according to the nature of the Ar group.

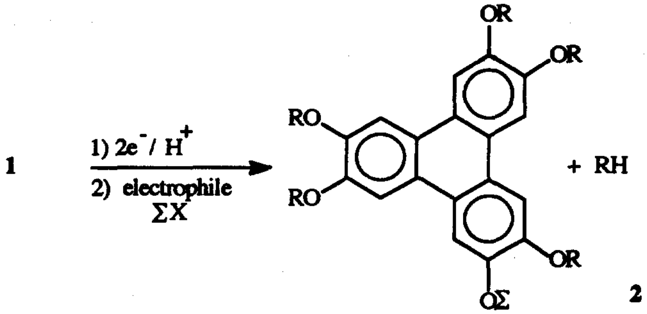
$$ArOR + \bar{e} \rightleftharpoons [\,ArRO\,]^{\cdot-} \qquad (E_1^0)$$

$$[ArOR]^{\cdot-} \xrightarrow{k_c} ArO^- \; + \; R^{\cdot}$$

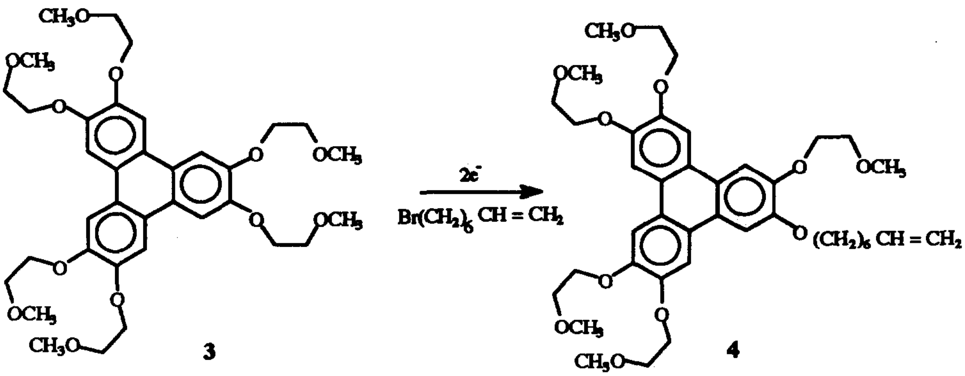
$$R^{\cdot} + [ArOR]^{\cdot-} \longrightarrow R^- \xrightarrow[\text{proton source}]{H^+} RH$$

Experimentally, it appears that all compounds 1 exhibit at least one two-electron step located at rather negative potential values. Owing to their weak ability to be reduced (low values of E_1^0), one has to use aprotic solvents like dimethylformamide or acetonitrile containing a tetralkylammonium salt as an electrolyte. The working cathode materials can be platinum or glassy carbon, but mercury is in most cases preferable. The k_c values can be calculated from voltammetry. For example : $k_c = 40\ s^{-1}$ with (I, R = Me) while it was found to be much larger ($k_c > 10^6\ s^{-1}$) with R = benzyl or allyl. The second two-electron step -when existing- was found to correspond to the specific reduction of the ArO^- anion produced , with the second cleavage (non regiospecific) of a carbon-oxygen bond.

Under the experimental conditions described here, the cleavage of 1 and the further reaction on the transient triphenylenoxide can be performed only *ex situ* owing to the effective electroactivity often presented by the electrophiles used. Moreover, the products 2 thus formed present generally a reducibility most comparable to that of the starting compound. Table 1 gathers the most significant results concerning the cathodic substitution of triphenylenes 2 with R = Me ($E_1^0 = -2.13$ V) and Bz ($E_1^0 = -2.00$ V). The reaction was generalized to other R's such as alkyl and polyether groups.



Such a procedure was also used in the case of 1 possessing polyether substituents. Below is given as an example the formation of 4 from 3 m.p. 123/124°C (yield 19 %). m/z = 724. 300 MHz RMN ^1H ($CDCl_3$) p.p.m. (TMS) : 7.8 - 8 (m, 6H) ; 5.7 - 5.9 (m, 1H) ; 4.9 - 5.1 (m, 2H) ; 4.4 (m, 10 H) ; 4.2 (t, $J^1{}_{H\text{-}H}$ = 6.62, 2H) ; 3.9 (m, 10H) ; 3.5 (s, 15H) ; 1.4 - 2.2 (m, 10H). Triphenylene[4] then contains a long unsaturated chain which allows its grafting to polymeric chains (e.g. to polysiloxanes in basic media[5] by means of hydrosilylation).



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Substrate	Electrophile ΣX	2 Isolated yield (%)	m.p. (° C)
1, R = CH2Ph	CH_3I	60	139-141
	C_2H_5I	56	143-144
	nC_4H_9I	53	158-159
	$CH_2 = CH - CH_2Br$	60	143-145
	$CH_2 = CH - (CH_2)_3Br$	56	152-153
	$CH_2 = CH - (CH_2)_6Br$	34	134-135
	$Br(CH_2)_3Br$	32	128-130
	AcOH	65	135-136
	Ac_2O	35	193-195
		20	128-131
1, R = CH3	$CH_2 = CH - CH_2Br$	30	195-196
	Ac_2O	29	244-246

Table 1 : Potentiostatic electrolyses performed on triphenylenes 1 (amount : 2 m. moles). Working cathode : stirred mercury pool (area : 5 cm^2). Use of a two compartment cell equipped with a glass-frit as a separator. Electrolyte : Dimethylformamide (DMF) containing 0.1 M NBu_4BF_4. Volume of the catholyte : 50 ml. Reference electrode : Ag / Ag I / I$^-$ 0.1 M system in DMF. Applied potential : - 2.0 V.

Electrolyses were always considered as completed when 2 ± 0.1 moles of electron per mole of 1 have passed. Electrophiles ΣX were then added in moderate excess (4 m. moles) and solutions refluxed (T = 150°C) overnight. Lastly, the catholyte was washed with water and extracted with ether.

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