A VERSATILE ANODIC SOURCE OF TRIPHENYLENES POSSESSING AT LEAST ONE IONOPHORIC SITE

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<u>Summary</u>: mixed anodic trimerization of aromatic orthodiethers and benzocrown ethers may lead to the formation of new triphenylenes possessing one (or two) complexing site(s).

The chemical¹ or electrochemical² oxidative conversion of aromatic orthodiethers M₁ into triphenylenes T(1, 1, 1) is now a rather well documented reaction³.



Such a trimerization process was successfully applied to the synthesis of new liquid crystals (when R is a long chain, either aliphatic or polyether). Potentialities of this reaction were also developed in the first synthesis of trimers possessing three complexing sites⁴ (e.g. anodic trimerization of relevant monobenzo-crown ethers). Lastly was recently shown⁵ the ability of dibenzocrown-ethers to polymerize anodically leading to a new family of materials (polytriphenylenes) exhibiting large ionophoric properties towards inorganic cations fast extracted from aqueous and organic solutions⁶.

Very recently was demonstrated⁷ the ability of diether M_1 to be electrochemically oxidized affording then new kinds of liquid crystals (synthesis of triphenylenes substituted both by OR_1 and OR_2 groups in well defined sequences).

The synthesis of liquid crystals possessing one or two complexing sites is of great interest since the stacking of those p-donors allowing the formation of ionophoric channels may be imagined (see e.g reference 9).Syntheses of structures of that type by classical means (e.g. from hexahydroxytriphenylene) no reported so far would be obviously long and difficult.

We present for the first time, the formation of trimers T $_{(1, 1, 2)}$ and T $_{(1, 2, 2)}$ according to the scheme below :





Experimentally, oxidation potentials of the different orthodiethers monomers are very close (of the order of 1.02 Volt vs Ag/AgNO₃ 0.1 M in acetonitrile). Oxidation of a monomer mixture including crown ethers M₂ leads essentially to trimers $T_{(1, 1, 2)}$ and $T_{(1, 1, 1)}$. Surprisingly under those experimental conditions trimers $T_{(2, 2, 2)}$ are not formed. $T_{(1, 2, 2)}$ appears to be produced only in trace amounts (evidenced by mass spectroscopy). On the contrary, trimers $T_{(2, 2, 2)}$ can be easily formed when electrolyzing the corresponding monomers M₂ alone⁸.

The method reported (here detailed with R: Me) can be now considered as a potential and facile source of triphenylenes possessing two functionalized R groups and other complexing sites.

EXPERIMENTAL

Electrolyses are carried out on 300 mg of monomer mixture in equal molar concentration in a Ushaped two-compartment cell (total volume 120 ml). Solvents and supporting electrolytes are carefully purified prior to use, according to previously described procedures^{6,7}.

The working electrode is a platinum sheet (area: 10 cm²), the counter electrode is made of a glassy carbon rod and potentials are referred to Ag/AgNO₃ 0.1 M system in acetonitrile.

Potentiostatic preparative electrolyses lead to trimers either insoluble or soluble in the anolyte. In the first case, a paramagnetic and conducting anodic deposit grows progressively on the anode

surface and has to be peeled away from platinum. After being filtered and rinsed by technical acetonitrile, those mixed valency salts are readily reduced by triethylamine.

In the absence of solid deposit onto the anode, the anolyte is taken from at the end of the electrolysis and then directly treated with triethylamine. After extraction with ether, the mixture is then purified by column chromatography.

| Entry rf | M1 | M ₂ | Ep ₁ (V) | Ep2 (V) | E _{applied} | Total yield (%) | T(_{1,1,1}) ratio (%) | T(1,1,2) ratio (%) | T(1,2,2) ratio (%) | T(2,2,2) ratio (%) |
|-------------|---------------------------------------|----------------|------------------------|------------|----------------------|-----------------------|---------------------------------------|--------------------------|--------------------------|--------------------------|
| 1 | Q ach, | ¢ [] | 1.05 | 1.04 | 1.010 | 26 | 47 | 53 | traces | - |
| 2 | QCH, | ¢~~> | 1.05 | 1.04 | 1.010 | 22 | 44 | 56 | | |
| 3 | $\operatorname{OCH}_{\mathrm{OCH}_3}$ | | 1.05 | 1.06 | 1.03 | 18 | 52 | 48 | traces | - |
| 5 | OC CCH | ¢ (~)> | 1.06 | 1.04 | 1.00 | 10 | 60 | 40 | - | |

<u>Table 1 :</u> Mixed electrolyses of monomers M_1 and M_2 . Ep₁ and Ep₂ represent peak potentials of monomeres -10⁻³ M- at a platinium mocroelectrode with a sweep rate of 0.1 V.s⁻¹.All yields mentionned in the table are isolated yields.

For entries 1, 2, 3 and 4, the monomer concentrations are 9.85, 8.88, 8.08 and 7.43 10-4 M respectively.

Entry n°1 : eluent : methylene chloride/acetone (30/70 v/v).

Column phase : silica gel (Merck 60 G).

T(1, 1, 1): m/z = 408; 60 MHz NMR (CDCl₃) δ ppm (TMS) : 7.65 (s, 6H), 4.10 (s, 18H);

m.p. (methylene chloride-pentane) : 297° C.

 $T(1, 1, 2): m/z = 538; 300 \text{ MHz NMR (CD}_3\text{CN}) \delta \text{ ppm (TMS)} : 7.99 (s, 2H), 7.87 - 7.88 (d, 4H), 4.44 - 4.47 (m, 4H), 4.06 (s, 12 H), 3.95 - 3.98 (m, 4H), 3.72 - 3.79 (m, 8H); m.p. (methylene chloride - pentane) > 310° C. T(1, 2, 2): m/z = 668.$

Entry nº 2 : eluent : methylene chloride/ethanol (92/8 v/v). Silica gel.

T(1, 1, 1) : see entry n° 1 T(1, 1, 2): m/z = 582; 300 MHz NMR (CD₃CN) δ₁ppm (TMS) : 7.88 (s, 4H), 7.87 (s, 2H), 4.43 - 4.46 (m, 4H), 4.04 - 4.05 (d, 12 H), 3.59 - 4.00 (m, 16H); m.p. (methylene chloride - pentane) : 277° C.

Entry nº 3 : eluent : methylene chloride/methanol (99/1 v/v)

on alumina gel column.

T(1, 1, 1) see entry n°1

T(1, 1, 2) m/z = 626; 300 MHz NMR (CDCl₃) δ ppm (TMS) : 8.05 (s, 2 H), 7.88 - 7.89 (2s, 4H), 4.24 - 4.27 (t, 4 H), 3.84 - 3.87 (t, 4 H), 3.43 - 3.73 (m, 28 H); m.p. (methylene chloride - pentane) : 146° C.

Entry n° 4 : eluent : methylene chloride/acetone (8/2 v/v) and then methylene chloride/methanol (95/5 v/v). Silica gel. T(1, 1, 1) m/z = 672; 300 MHz NMR (CDCl₃) δ ppm (TMS) : 7.88 (s, 6 H), 4.39 (t, 12 H), 3.89 (t, 12 H), 3.52 (s, 18 H); m.p. (methylene chloride - pentane) : 161° C. T(1, 1, 2) : m/z = 758; 300 MHz NMR (CDcl₃) δ ppm (TMS) : 7.88 (s, 2H), 7.84 (s, 2H), 7.72 (s, 2H), 4.35 - 4.40 (m, 12H), 4.02 - 4.06 (m, 4H), 3.87 - 3.91 (m, 8H), 3.79 - 3.83 (m, 4H), 3.69 - 3.73 (m, 8H), 3.52 (2s, 12H); m.p. (methylene chloride - pentane) : 100° C.

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- 8) The trimer of benzo-18-crown-6 has been prepared by our group by electrolysis in acetonitrile with isolated yield of 20 % by using the present recipe (case of an insoluble product)-300 MHz NMR (CD₃CN) δ ppm (TMS) 7.84 (s.6H), 4.37-4.41 (m,12H), 4.04-4.07 (m,12H), 3.82-3.85 (m,12H), 3.74-3.77 (m,12H); m.p. (methylene chloride pentane): 160°C. Work presently in progress shows also that anodic trimerization of benzo -21- crown 7 is also feasible.
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