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Improved protocol for the synthesis of functionalized triphenylene ketals

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Abstract

The trimerization of catechol ketals towards functionalized triphenylene ketals by anodic oxidation is presented. The described protocol is superior in yield and environmental aspects to all known procedures.

Keywords: triphenylene; oxidation; electrochemistry; supramolecular chemistry.

Receptors based on functionalized triphenylene ketals lead to novel systems with a high potential for supramolecular chemistry.[1] The triphenylene core with directed functional groups accomplishes a tripodal platform. The distances of 10–11 Å between the side chains generate C_3-symmetric clefts which offer advantages in size and rigidity over existing systems. Recently, a direct synthesis for such triphenylene ketals was reported.[2] The corresponding catechol ketals are oxidative trimerized by molybdenum pentachloride. Other transition metal reagents failed since the cleavage of the ketal moiety was faster than the oxidative step. Furthermore, we found that molybdenum pentachloride acts as an one-electron oxidant and therefore, 2 equivalents of the oxidizing reagent are required for the carbon–carbon bond formation.[3] Anodic oxidation of catechol derivatives seems ideal for the synthesis of triphenylene ketals because no transition metal cations are involved, which could lead to cleavage of the ketal moiety. The first example for an anodic trimerization of catechol derivatives was demonstrated by Parker.[4] Employing this methodology in a specific electrolysis cell Simonet and co-workers established the trimerization of catechol ethers to the corresponding triphenylene derivatives.[5] The moderate and even poor yields caused by low oxidation potential of the products and subsequent decomposition of the radical cations made this synthesis unattractive from the beginning. Since having a specific interest in a large-scale access to functionalized triphenylene ketals we were prompted to develop a non-problematic synthesis thereof.

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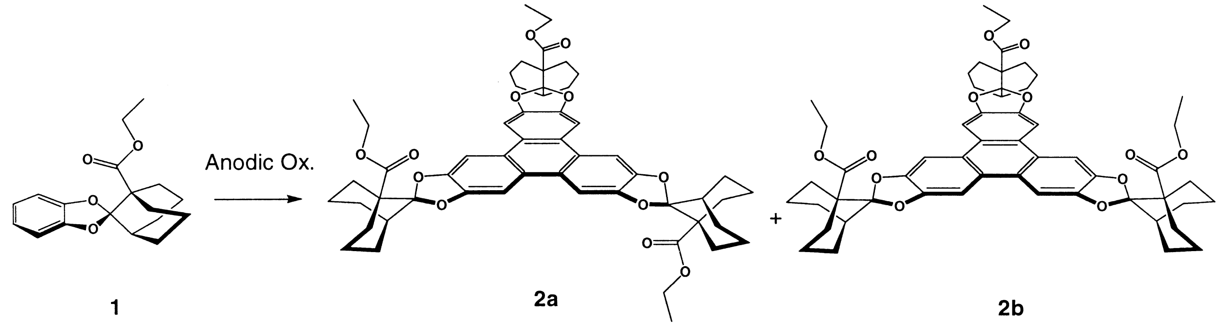
We report a new simple protocol for the anodic oxidation of catechol ketals forming triphenylene ketals. The electrolysis is done under very simple galvanostatic conditions using platinum sheets as electrode material. Consequently, no expensive arrangement of potentiostats and reference electrodes is required. Best results were obtained in acetonitrile and tetrabutylammonium tetrafluoroborate as electrolyte. The triphenylene products precipitate during electrolysis preferably on the cooler parts of the cell. Blocking of the platinum surfaces by precipitated material is not observed. Usually the solid products float as a light sandy material in the cell.



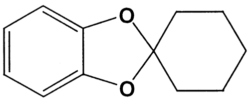
A maximum amount of triphenylenes is obtained when the conversion reaches about 80%. This corresponds to a current efficiency of 69%. The triphenylenes are easily isolated. Best results are obtained for the sterically hindered bicyclic spiro ketal **1**.[1] The starting material is easily recovered and the total loss of ketalized material is less than 5%. Since the *anti,anti,syn*-isomer **2a** is less soluble than the all-*syn* **2b**, it crystallizes first and the isomeric ratio turns from the statistical 3:1 mixture of **2a** to **2b** into an approximately 4:1 ratio. Interestingly, a higher content of **2a** indicates an isomerization under cationic conditions. Under strong acidic conditions **2a** was transformed into the statistical mixture of **2a** to **2b** which made the desired **2b** accessible in multigram scales.

Using the common electrolytes for aryl–aryl couplings such as CH_2Cl_2/TFA only resulted in a tarry product (Table 1, entry 1). Improvement was achieved with inert ammonium salts. In CH_2Cl_2 the triphenylene products remain in solution and many decomposition products are observed. When acetonitrile is used only a small amount of degraded material is observed. Shortly after starting the reaction **2** is precipitated. The continual removal of the triphenylene products prevents their further oxidation and successive side reactions leading to strongly colored compounds.

Table 1
Variation of the electrolyte in the synthesis of **2a**/**2b**

Entry	Electrolyte	Conversion	**1** (recovered)	2a/2b
1	CH_2Cl_2/TFA	100 %	--	--
2	CH_2Cl_2/TBABF$_4$	79 %	21 %	47 %
3	CH_3CN/TBABF$_4$	82 %	18 %	77 %

The process and work-up involves the recovery of the acetonitrile, and crystallization can be done in an environmentally friendly mixture of ethanol and ethyl acetate. The simple and reliable protocol offers an up-scale to 20 g batches of triphenylene ketals. This is one of the rare examples where electrochemistry is superior to conventional chemistry.



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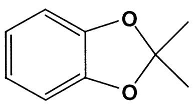

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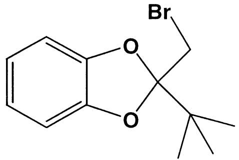

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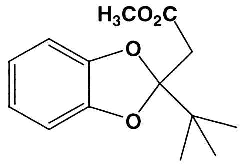

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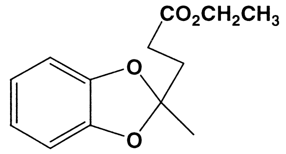

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Good conversions and satisfactory yields are achieved where the products crystallize during electrolysis (Table 2, entries 1–3). The triphenylene ketals derived from **6** or **7** are soluble in acetonitrile and obtained in decreased yields. When the products do not precipitate the conductivity rises during electrolysis indicating that ionic species are generated. The current efficiency then drops tremendously.

Table 2
Anodic oxidation of catechol ketals in $CH_3CN/TBABF_4$

Entry	Catechol ketal	Conversion	Triphenylenes[9]
1	**3**	88 %	62 % (**8**)
2	**4**	-- [a]	45 % (**9**)
3	**5**	77 %	51 % (**10**)
4	**6**	65 %	31 % (**11**)
5	**7**	55 %	20 % (**12**)

[a] Since the catchol ketal is too volatile no data are available.

In conclusion, triphenylene ketals are easily synthesized by anodic oxidation using a simple galvanostatic procedure. Best results are obtained when the synthesized triphenylene ketals are sparingly soluble in acetonitrile. Beneficial are sterically hindered ketal moieties which have no polar and flexible functional groups which decrease the ability to crystallize the triphenylene products. Since anodic oxidation chemistry is compatible with a variety of moieties which do not tolerate molybdenum pentachloride this procedure will be suitable for the direct synthesis of novel receptors.[6] The products of entries 1–5 in Table 2 are excellently soluble in non-polar solvents as diethyl ether. Since the transketalization of benzodioxoles is easily accomplished the reported products may serve as soluble equivalents for 2,3,6,7,10,11-hexahydroxytriphenylene for the synthesis of discotic mesogens[7] or optoelectronic devices.[8]

Acknowledgements

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9. **General procedure:** 10 mmols of catechol ketal are dissolved in 25 mL of 0.1 M tetrabutylammonium tetrafluoroborate in acetonitrile. The electrolysis is done under an inert atmosphere in a standard electrolysis cell equipped with two platinum sheets as electrodes (2×4 cm^2). The reaction is performed with a current density of 0.016 Acm^{-2} at 20°C. After 2700 C are applied the mixture is evaporated to dryness recovering the acetonitrile. The residue is dissolved in a small amount of ethyl acetate and slowly diluted with aqueous ethanol. The triphenylenes precipitate and are filtered off. The starting material can be recovered by column chromatography of the filtrate. When the reaction is performed with **5**–**7** the triphenylenes are isolated directly by column chromatography on silica (cyclohexane/ethyl acetate). All triphenylenes are characterized by ^{1}H and ^{13}C NMR, mass spectrometry and micro analysis. For identification of **2a**/**2b**, see Ref. 1 and for **9**, see: Ringdorf, G.; Bjørnholm, T.; Bechgaard, K. *Acta Cryst.* **1989**, *C45*, 267–269. Selected analytical data: compound **8**: ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) = 1.48–2.32 (m, 30H), 7.65 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) = 23.7, 25.0, 35.8, 101.5, 119.4, 124.9, 147.9; compound **10** (both isomers): ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) = 1.16 (s, 27H), 3.96 (s, 6H), 7.73 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) = 24.9, 35.2, 39.7, 100.0, 120.9, 125.9, 149.4; compound **11** (all-*syn*): ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) = 0.96 (s, 27H), 2.90 (s, 6H), 3.24 (s, 9H), 7.52 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) = 24.7, 39.5, 41.4, 52.2, 100.5, 121.8, 124.9, 149.2, 169.4; compound **12** (both isomers): ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) = 1.20 (t, $^3J = 7.2$ Hz, 9H), 1.60 (s, 9H), 2.28 (m, 6H), 2.46 (m, 6H), 4.09 (q, $^3J = 7.2$ Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) = 14.1, 24.7, 28.3, 34.4, 60.6, 101.1, 118.8, 124.6, 147.6, 172.6.