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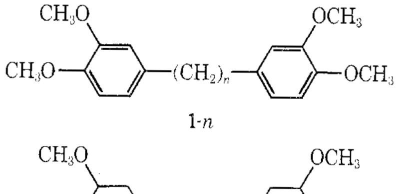
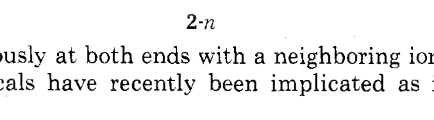
Electrosynthesis of Medium- and Large-Sized Rings by Oxidative Cyclization of Bis(3,4-dimethoxyphenyl)alkanes

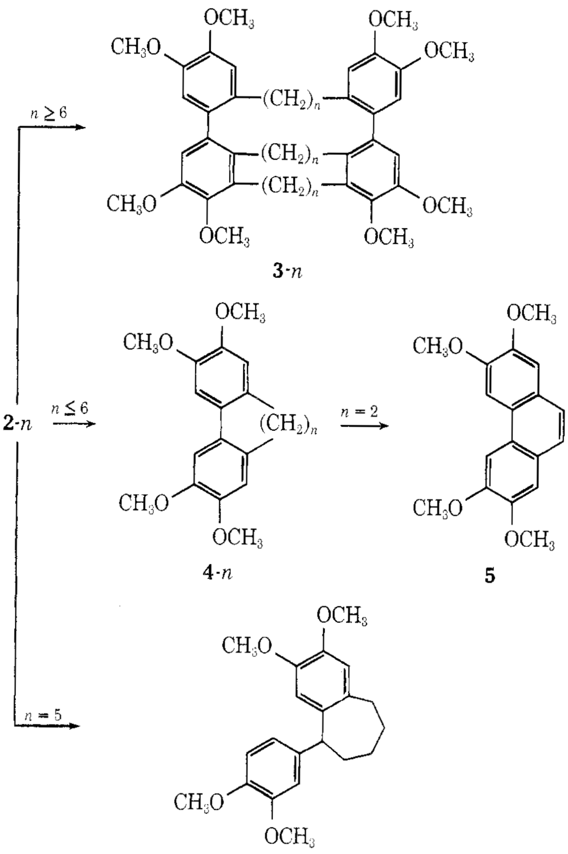
Summary: On anodic oxidation in trifluoroacetic acid (TFA)-dichloromethane, diarylalkanes, Ar(CH$_2$)$_n$Ar where Ar = 3,4-dimethoxyphenyl and $n \geq 6$, undergo a novel dimerization–cyclization reaction with formation of a ($2n + 8$)-membered ring compound (**3**-n).

Sir: We report the anodic synthesis of cyclic compounds containing rings with as many as 40 members starting from the bis(3,4-dimethoxyphenyl)alkanes (**1**-n). These reactions involve two-electron oxidations to give the intermediate dication diradicals (**2**-n) which undergo coupling simultaneously at both ends with a neighboring ion. Dication diradicals have recently been implicated as intermediates in the intramolecular cyclization of methoxybibenzyls.[1] While the synthesis of medium- and large-sized rings has its own inherent interest, the results presented here are particularly novel since all previous attempts to prepare such compounds by anodic coupling reactions have been entirely unsuccessful.[2]


1-*n*


2-*n*

Scheme I



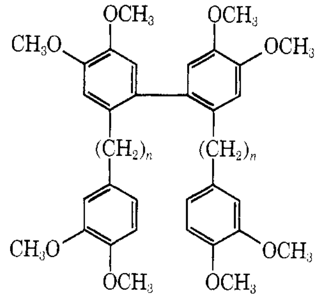
The synthesis were carried out by anodic oxidation of the substrates (5.0 mmol) in TFA–dichloromethane (1:3) containing n-Bu$_4$NBF$_4$ (1 g in 200 ml of solvent) in a closed two-compartment cell. Constant current (current density 0.16 mA/cm^2) oxidation was carried out at a platinum anode (150 cm^2) at −20° under nitrogen until 3.0 Faradays/mol had been passed. Zinc dust (3 g) was added and stirring was continued for an additional hour at −20°. After work-up, the oily residue was chromatographed on silica gel (200 g, toluene–ethyl acetate gradient, 25-ml fractions). The fractions were analyzed by tlc and nmr and mass spectroscopy. The results, along with those obtained by oxidation with manganic tris(acetylacetonate)[3,4] (MTA) are summarized in Table I.

Large-ring compounds (**3**-n) are only formed on the oxidation of compounds containing a saturated chain of six or more carbons. As indicated in Table I, both the yield and the nature of the oxidation products of **1**-n depend dramatically upon the carbon chain length. In spite of this, we feel that the initial oxidation product is *2*-n in all cases.[5] The reactions which the various dication diradicals (**2**-n) undergo are summarized in Scheme I. When n is 4 or smaller intramolecular cyclization giving the bridged biphenyls (**4**-n) is the exclusive reaction pathway. In the specific case of $n = 2$, the phenanthrene **5** is the product isolated.[1] The case where $n = 5$ (**1**-5) is unique. Cyclization here occurs between one ring and the position α to the other ring to give **6**. It is of interest that the yield of **3**-n is low for $n = 6$ or 7, reaches a maximum at $n = 8$ or 9, and diminishes sharply at $n = 16$. Also at $n = 16$ the

Table I
Oxidation of Bis(3,4-dimethoxyphenyl)alkanes (1-*n*) in TFA–Dichloromethane

	Anodic oxidation		MTA oxidation,[a]			
Compd	Conversion (%)	Products (yield %)	products (yield %)	Mp,[b] °C	Nmr, δ (ppm)[c]	*m/e*[d]
1-1	98	**4-1** (95)	**4-1** (45)	183–184	4.03 (s, 3 H), 4.18 (s, 3 H), 4.20 (s, 2 H), 6.77 (s, 2 H), 7.20 (s, 2H)	286 (M^+)
1-2	95[e]	**5** (95)[e]	**4-2** (45), **8** (19)	211–213 (for **8**)	2.80 (m, 2 H), 3.92 (s, 12 H), 4.00 (s, 12 H), 4.08 (m, 2 H), 6.75 (s, 4 H), 7.15 (s, 4 H) (for **8**)	598 (M^+)
1-3[f]	98	**4-3** (94)	**4-3** (60)	158–159	2.40 (m, 6 H), 3.91 (s, 12 H), 6.80 (s, 2 H), 6.96 (s, 2 H)	314 (M^+)
1-4	97	**4-4** (93)	**4-4** (90)	115–116	1.10–2.90 (m, 8 H), 3.81 (s, 6 H), 3.82 (s, 6 H), 6.73 (s, 2 H), 6.76 (s, 2 H)	328 (M^+)
1-5[g]	95	**6** (38)	**6** (25)	Oil	1.93 (m, 6 H), 2.80 (m, 2 H), 3.63 (s, 3 H), 3.86 (t, 9 H), 6.33 (s, 1 H), 6.78 (m, 4 H), 4.16 (m, 1 H)	342 (M^+)
1-6	96	**3-6** (4)	Only polymers	120–122	1.16 (m, 16 H), 2.40 (m, 8 H), 3.83 (s, 12 H), 3.95 (s, 12 H), 6.63 (s, 4 H), 6.80 (s, 4 H)	712 (M^+) 356 (M^{2+})
1-7	94	**3-7** (12)	Only polymers	129–130	1.16 (m, 20 H), 2.32 (m, 8 H), 3.83 (s, 12 H), 3.95 (s, 12 H), 6.64 (s, 4 H), 6.80 (s, 4 H)	740 (M^+) 370 (M^{2+})
1-8	100	**3-8** (43)	**3-8** (8)	153–154	1.16 (m, 24 H), 2.30 (m, 8 H), 3.83 (s, 12 H), 3.95 (s, 12 H), 6.65 (s, 4 H), 6.80 (s, 4 H)	768 (M^+) 384 (M^{2+})
1-9	100	**3-9** (42)	**3-9** (7)	93–94	1.31 (m, 28 H), 2.33 (m, 8 H), 3.83 (s, 12 H), 3.95 (s, 12 H), 6.66 (s, 4 H), 6.83 (s, 4 H)	796 (M^+) 398 (M^{2+})
1-10	100	**3-10** (38)	**3-10** (5)	133–134	1.16 (m, 32 H), 2.36 (m, 8 H), 3.83 (s, 12 H), 3.95 (s, 12 H), 6.66 (s, 4 H), 6.83 (s, 4 H)	824 (M^+) 412 (M^{2+})
1-16	100	**4-16** (16), **3-16** (8)	**4-16** (4)	95–97 (for **4-16**) 60–62 (for **3-16**)	1.21 (m, 56 H), 2.28 (m, 8 H), 3.78 (s, 12 H), 3.87 (s, 12 H), 6.55 (s, 4 H), 6.71 (s, 4 H) (for **3-16**)[h]	992 (M^+, **3-1**) 496 (M^{2+}, **3-1**) 496 (M^+, **4-16**)

[a] Three mole of MTA per mole of substrate in TFA–dichloromethane was added during 1 hr to a cooled (−20°) 25 m*M* solution of the diarylalkane in TFA–dichloromethane under N_2 with stirring. When all of the substrate had been consumed (tlc) the reaction mixture was worked up as the electrolysis mixtures. [b] Compounds **4-1**, **4-3**, and **4-4** were recrystallized from ethanol and compounds **3-6** to **3-10**, **3-16**, and **4-16** from ether–pentane (4:1). All new compounds gave satisfactory elemental analysis. [c] Recorded in $CDCl_3$ with TMS internal standard. In the starting compounds (**1-*n***) the CH_2 protons appear at 1.43 [m, (2*n* − 4) H] and 2.50 (m, 4 H), the methoxy protons at 3.85 (br s, 12 H), and the aromatic protons at 6.70 ppm (narrow m, 6 H). [d] For all compounds M^+ was the base peak. For all compounds **3-*n*** a strong peak appeared at M/2 identified as M^{2+} by the presence of a C-13 satellite at M/2 + 0.5. [e] From ref 1. [f] With this particular compound the same result was obtained in acetonitrile buffered with solid sodium carbonate. [g] Only 2 Faradays of current/mol of substrate was passed through the cell in this experiment. [h] The 60-MHz nmr for **4-16** is identical with that of **3-16**.



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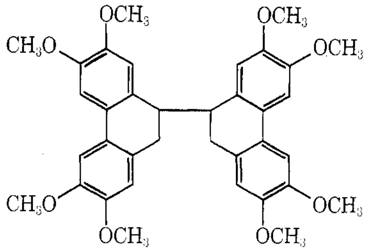
intramolecular cyclized product, **4-16**, is obtained in moderate yield.[6]

That the dication diradicals (**2-*n***) are the initial oxidation products of **1-*n*** does not in itself explain why good yields of the cyclic dimers (**3-*n***, *n* = 8–10) are obtained. A random orientation of the molecules would bring about intermolecular coupling and the formation of polymeric products. This appears to be the case for *n* = 6 or 7 where polymeric materials account for most of the substrate consumed. In the cases where high yields are obtained (*n* = 8–10), it appears that the saturated carbon chains orient in a parallel fashion in the relatively polar medium.

In general, the yields of cyclized products are lower when MTA is the oxidant. This reflects the difference between a concerted reaction involving **2-*n*** and a reaction involving stepwise oxidation of the two aryl groups in **1-*n***[7] and stepwise formation of the bonds in **3-*n***. Another difference in the anodic and MTA oxidations is seen for *n* = 2. Anodically, **4-2** is oxidized cleanly to **5** while MTA brings about formation of the intermolecular dimer **8**.



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Application of this novel reaction to synthesis of other large rings, in particular crown ethers, is presently under investigation.

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References and Notes

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(4) Thallium trifluoroacetate and $[Fe(DMF)_3Cl_2][FeCl_4]$ where DMF means dimethylformamide were also tried and found inferior to MTA.

(5) Voltammetric data indicates that a saturated carbon chain separating two identical electroactive aryl groups insulates the two groups from each other and allows both groups to lose an electron at about the same potential giving the dication diradical.[1] The same argument applies equally well to the compounds discussed here.

(6) It should be noted that it is impossible to distinguish between structures **3**-*n* and **4**-*n* by elemental analysis or nmr spectroscopy and all compounds were first believed to have structure **4**-*n* until both molecular ions and doubly charged ions were found in the high resolution mass spectra.

(7) Simultaneous oxidation of both aryl groups of **1**-*n* would require an unlikely trimolecular reaction.

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