trary to the assumption that a compound like cyclobutanone, in which the bond angle is deformed by 30° (from the usual 120 to 90°), should be much more strained than a compound like cyclobutane or cyclobutanol, in which the deformation of the bond angle is only 19° (from 109 to 90°). The result is in agreement with the finding that the CCC bond angle of the carbonyl group in cyclobutanone is very close to 90° (90° 38′),[32] with the results of Wiberg and Fenoglio[33] that cyclobutene with two sp^2 carbon atoms in the ring is only moderately more strained than cyclobutane, and with the finding of Turner and coworkers that the heat of hydrogenation of methylenecyclobutane[34] (ΔH = -29.4 kcal/mol) is only moderately higher than for methylenecyclopentene[35] (ΔH = -26.8 kcal/mol). It is, however, noteworthy that while the introduction into the cyclobutene ring system of an sp^2 carbon atom which is part of a carbon–carbon double bond does result in a measurable increase in the total strain energy, the effect of the carbonyl sp^2 carbon is in the opposite direction.

Table XI. Enthalpies of Formation and Strain Energies (kcal/mol) per Cyclobutane, Cyclobutanol, and Cyclobutanone at 25°

	$-\Delta H_f{}^\circ{}_g$		Total
Compd	Exptl	Calcd[a]	strain energy
Cyclobutane	-6.30^b	19.8	26.1
Cyclobutanol	34.6^c	59.7	25.1
Cyclobutanone	21.9^d	46.4	24.5

[a] For strain-free compounds.[29] [b] Reference 28. [c] From heat of combustion $-\Delta H_c{}^\circ{}_l$ = 601.87 ± 0.16 kcal/mol and heat of vaporization ΔH_v = 13.0 kcal/mol. [d] From $-\Delta H_c{}^\circ{}_l$ = 549.89 ± 0.15 kcal/mol and ΔH_v = 9.4 kcal/mol.

The finding that the ring strain in cyclobutanol and in cyclobutanone are about equal thus makes the oxidation rates obtained in this study and earlier by Kuivila and Becker[18a] readily understood: as the reaction does not lead to an increase in ring strain, there is no reason to expect cyclobutanol to be less reactive than related strain-free alcohols.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the U. S. Army Research Office, Durham, for generous support of this research. We are greatly indebted to Dr. D. D. Wagman and Mr. J. Miner of the National Bureau of Standards for the measurement of the heats of combustion.

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(32) A. Bauder, F. Tank, and H. H. Günthard, *Helv. Chim. Acta*, **46**, 1453 (1963). If considerably more energy were required to deform the carbon–carbon bonds of a carbonyl carbon than of a methylene carbon, then the bond angle at the carbonyl group should have been considerably greater, which would at the same time reduce the bond angle at the two neighboring methylene groups.

(33) K. B. Wiberg and R. A. Fenoglio, *J. Amer. Chem. Soc.*, **90**, 3395 (1968). Using the same method[29] for the calculation of the enthalpy of formation for the strain-free compound employed in Table XI, a value of 29.8 kcal/mol for the strain energy of cyclobutene is obtained. This value is somewhat greater than the value of 28.5 kcal/mol estimated by the authors.

(34) R. B. Turner, P. Goebel, B. J. Mallon, W. von E. Doering, J. F. Coburn, Jr., and M. Pomerantz, *ibid.*, **90**, 4315 (1968).

(35) R. B. Turner and R. H. Garner, *ibid.*, **80**, 1424 (1958).

Anodic Oxidation of Methoxybibenzyls. Products and Mechanism of the Intramolecular Cyclization

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Contribution from the Department of Organic Chemistry, Lund Institute of Technology, Chemical Center, Lund 7, Sweden, and the Department of General and Organic Chemistry, The H. C. Ørsted Institute, University of Copenhagen, DK-2100 Copenhagen, Denmark. *Received February 6, 1973*

Abstract: The intramolecular cyclization of a number of methoxy-substituted bibenzyls and bis(3-methoxyphenyl)methane was shown to take place upon anodic oxidation in acetonitrile or in media containing trifluoroacetic acid (TFA). Yields are low in the former solvent due to the fact that the cyclized products are more easily oxidized than their precursors and the oxidation products are not stable. In the presence of TFA, the cation radicals derived from the oxidation of the cyclized products are stable and, thus, after reduction the dihydrophenanthrenes or fluorene may be isolated in high yield. Potential step cyclic voltammetry was used to provide evidence that the reactions occur by oxidation to the dication diradicals which couple and eliminate protons. In acetonitrile, voltammetry was used to show that the coupling reaction is markedly sensitive to the conditions and appears to be catalyzed by H_3O^+, in the absence of which no coupling was observed.

Coupling reactions are perhaps the area in which electrochemical synthesis can be of the most practical importance. The coupling of aromatic nuclei by anodic oxidation has recently been the subject of several investigations. In a preliminary communication of this work, the intramolecular coupling reaction of 3,3′,4,4′-tetramethoxybibenzyl (**2**) in acetonitrile to the corresponding dihydrophenanthrene was reported.[2] More recently, coupling of compounds structurally similar to **2** has been described by two groups of workers.[3] Anodic intramolecular phenol coupling has been shown to be useful in the alkaloid

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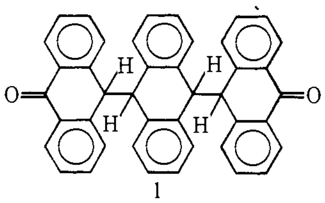
(1) (a) Lund Institute of Technology; (b) University of Copenhagen.

(2) A. Ronlán and V. D. Parker, *Chem. Commun.*, 1567 (1970).

(3) (a) M. Sainsbury and R. F. Schinazi, *J. Chem. Soc., Chem. Commun.*, 718 (1972); (b) L. L. Miller, F. R. Stermitz, and J. R. Falck, *J. Amer. Chem. Soc.*, **93**, 5941 (1971).

field.[4] The intramolecular coupling of simple aryl ethers is a high yield reaction pathway when anodic oxidation is carried out in media containing TFA.[5]

The mechanism of anodic coupling reactions of aromatic compounds is open to question. An expected reaction pathway is the dimerization of anodically generated cation radicals. In the case of intramolecular coupling this reaction pathway would have to involve the coupling of dication diradical intermediates. Another pathway, involving the attack of anodically generated cation radical on unoxidized substrate, has been proposed for the anodic coupling of alkylbenzenes.[6] There is evidence that such a pathway does exist in that a major product of the anodic oxidation of anthracene in aqueous acetonitrile is the trimer (**1**) in which the central anthracene unit is in unoxidized form inserted between two oxidized units.[7]



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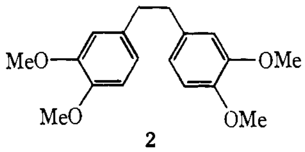
In this paper we extend the preliminary acetonitrile work[2] to include the oxidation of several other methoxy-substituted bibenzyls and bis(3-methoxyphenyl)methane and report results obtained in dichloromethane–TFA which indicate that the latter medium is suitable for the anodic synthesis of the corresponding dihydrophenanthrenes from the methoxybibenzyls.

Results

Oxidation of 3,3′,4,4′-Tetramethoxybibenzyl (2). The anodic oxidation of 2 in acetonitrile was accompanied by the formation of **4** in low yield. The most likely reaction sequence resulting in the formation of **4**



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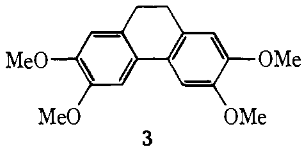

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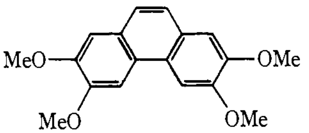

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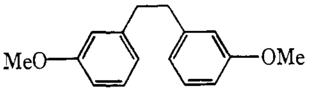
involves oxidative cyclization of **2** to the dihydrophenanthrene (**3**). Thus the oxidation of **3** in acetonitrile was investigated and the oxidative dehydrogenation to **4** was found to take place in nearly quantitative yield. In dichloromethane–TFA (4:1), **4** could be obtained in nearly quantitative yield directly from **2** by allowing the electrolysis to run until 4 F/mol had been consumed.

Oxidation of 3,3′-Dimethoxybibenzyl (5). The results of the oxidation of **2** suggested that intramolecular cyclization accompanied by the formation of the 4,4′-dimethoxybiphenyl structural moiety should be general for properly substituted substrates. However, only intractable tars were obtained from anodic oxidation of **5** in acetonitrile. On the other hand, oxidation in dichloromethane–TFA (4:1) resulted in the formation of **6** and its further oxidation product (**7**) which is stable in that medium. After cathodic reduction of **7**, **6** was obtained in high yield.



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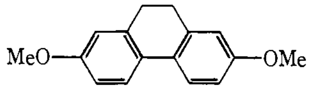

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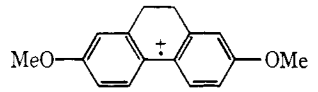

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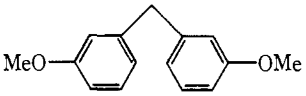
Oxidation of Bis(3-methoxyphenyl)methane (8). A low yield of **9** was obtained upon oxidation of **8** in acetonitrile. Here again, dichloromethane–TFA (4:1) proved to be a suitable medium to achieve the intramolecular cyclization reaction, and after reduction of any overoxidation product (**10**), 2,7-dimethoxyfluorene (**9**) was obtained in high yield.



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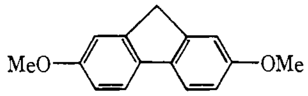

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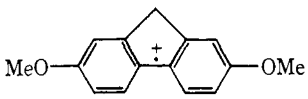

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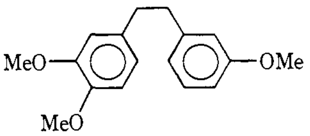
Oxidation of 3,3′,4-Trimethoxybibenzyl (11). Results of potential step cyclic voltammetry on the oxidation of **11** in either acetonitrile or dichloromethane–TFA (4:1) suggested that it might be possible to obtain both an intramolecular and an intermolecular coupled product depending on the anode potential applied during oxidation. Thus, oxidation of **11** at very low current density at −30° in dichloromethane–TFA (4:1) resulted in the formation of the dimer (**12**) which was isolated in 50% yield. As expected from the voltammetric results, oxidation at higher current density resulted in the formation of the intramolecular cyclization product **13** as well as **12**. However, **13** could not be isolated from the latter experiment since it is oxidized to the corresponding dication at +1.21 V which rapidly deprotonates to give the corresponding phenanthrene.



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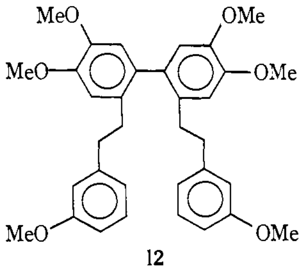

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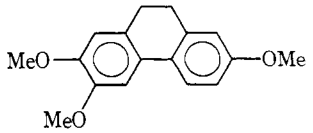

13

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(4) J. M. Bobbitt, H. Hagi, S. Shibuya, and J. T. Stock, *J. Org. Chem.*, **36**, 3006 (1971), and references cited therein.

(5) K. Bechgaard, O. Hammerich, N. S. Moe, A. Ronlán, U. Svanholm, and V. D. Parker, *Tetrahedron Lett.*, 2271 (1972).

(6) K. Nyberg, *Acta Chem. Scand.*, **25**, 2499 (1971).

(7) V. D. Parker, *Acta Chem. Scand.*, **24**, 2757 (1970).

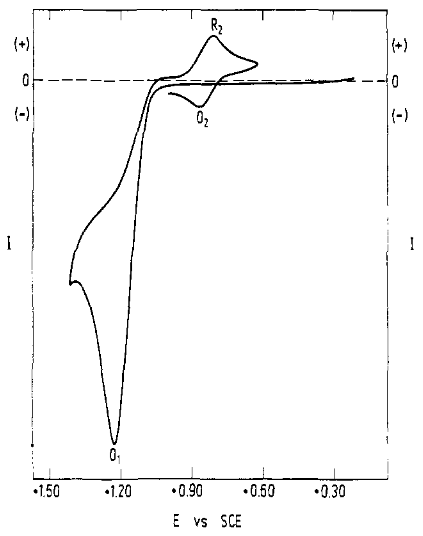


Figure 1. Cyclic voltammogram for the oxidation of 3,3′,4,4′-tetramethoxybibenzyl (**2**) in acetonitrile containing sodium perchlorate (0.1 *M*). Voltage sweep rate 86 mV/sec.

Table I. Voltammetric Data for the Anodic Cyclization of Bibenzyls

Compd[a]	Solvent	Peak potentials[b] O_1	R_2	O_2
2	MeCN[c]	1.23	0.84	0.89
2	TFA–CH_2Cl_2[d]	1.42	1.04	1.10
5	MeCN[c]	1.62	1.01	1.07
5	TFA–CH_2Cl_2[d]	1.73	1.16	1.22
8	MeCN[c]	1.68	0.95	1.01
8	TFA–CH_2Cl_2[d]	1.81	1.27	1.34

[a] 1.0 m*M* solution. [b] Measured at 86 mV/sec *vs.* sce. [c] Containing sodium perchlorate (0.1 *M*). [d] Containing tetrabutylammonium tetrafluoroborate (0.25 *M*).

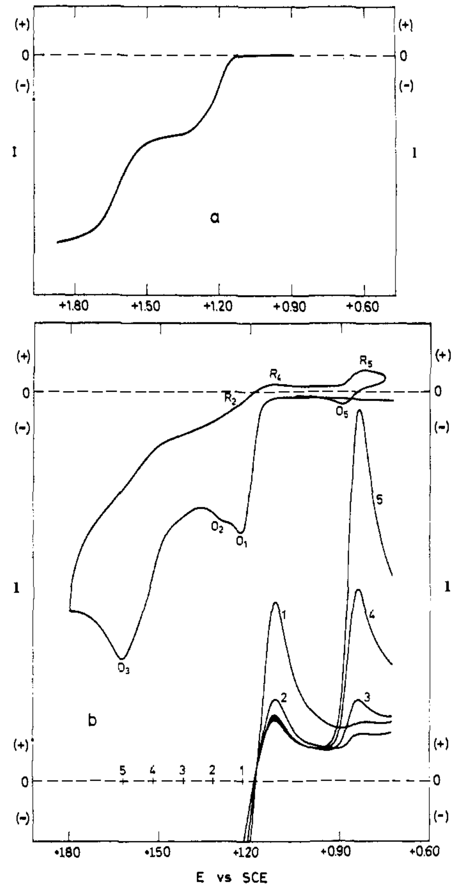
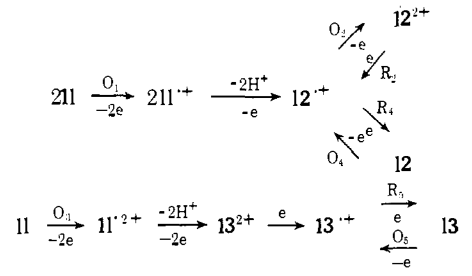


Figure 2. (a) Rde voltammogram for the oxidation of 3,3′,4-trimethoxybibenzyl (**11**) at −28° in acetonitrile containing sodium perchlorate (0.1 *M*). (b) Cyclic and potential step–sweep voltammogram under the same conditions as (a). Voltage sweep rate 86 mV/sec. Hold potentials: (1) +1.22 V, (2) +1.32 V, (3) +1.42 V, (4) +1.52 V, and (5) +1.62 V. The current amplification of the potential step voltammogram is ten times that of the cyclic voltammogram.

Scheme I



Voltammetry of the Symmetrically Substituted Bibenzyls. Cyclic voltammetry for **2**, **5**, and **8** in either acetonitrile or dichloromethane–TFA (4:1) showed on the initial anodic sweep that the substrate was oxidized irreversibly (O_1) and on the cathodic sweep a reduction peak (R_2) appeared which is due to reduction of the cation radical of the intramolecular cyclized product and the second anodic cycle gave in addition the oxidation peak (O_2) for the product. The voltammogram for **2** in acetonitrile, which is representative for all three compounds, is illustrated in Figure 1. Voltammetric data for both solvents are tabulated in Table I.

Voltammetry of 3,3′,4-Trimethoxybibenzyl (11). Since the results for the title compound are significantly different than for those of the symmetrically substituted compounds, they are treated here in a separate section. The cyclic voltammogram of **11** in acetonitrile at −28° is shown in the upper part of Figure 2b, and reactions occurring at each peak are summarized in Scheme I. Unlike, the other voltammogram (Figure 1), the initial anodic sweep unveils two major oxidation peaks (O_1 and O_3) as well as one minor peak (O_2). On the cathodic sweep, two small peaks and one larger peak are visible (R_2, R_4, and R_5). Potential step sweep voltammetry[8,9] was applied at various hold potentials ranging from O_1 to O_3. The procedure used was to step the potential to a predetermined value (marked with + on Figure 2b), hold for 30 sec, and then sweep in the cathodic direction. Two major oxidation products are observed depending upon the hold potential as indicated by the appearance of either R_4 or R_5 on the cathodic sweep. The first hold (E $\simeq$ O_1) gave rise to a large current at R_4 on the sweep while R_5 does not become significant until hold potentials on the second oxidation peak (O_3) are employed. These experiments suggested that the different behavior of **11** as compared to **2**, **5**, and **8** is a consequence of the fact that **11** has two different methoxy bearing rings with unequal ease of oxidation. It appeared reasonable to suppose that the ring bearing two methoxy groups should be dis-

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[8] L. Papachoudo, J. Bacon, and R. N. Adams, *J. Electroanal. Chem. Interfacial Electrochem.*, **24**, App 1 (1970).

[9] V. D. Parker and L. Eberson, *J. Amer. Chem. Soc.*, **92**, 7488 (1970).

charged at a potential similar to that of **2** (+1.23 V) while the second ring should lose an electron at a potential more anodic than **5** (+1.62 V). Since formation of **12** (which depletes the diffusion layer of **11**) is a rapid process at O_1, cyclic voltammetry at a stationary electrode is not a suitable technique to determine at what potential the dication of **11** is formed. Since the products of electrode processes are rapidly convected away from the electrode surface during rotating disk electrode (rde) voltammetry, this technique was suitable for the determination of the potential of the second charge transfer of **11**. Thus, the rde voltammetry of **11** (Figure 2a) showed two waves: $E_{1/2}{}^1 = +1.21$ V and $E_{1/2}{}^2 = +1.62$ V. Voltammograms of the intra- (**13**) and intermolecular (**12**) coupling products are shown in Figure 3. The cyclic voltammogram of **13** (Figure 3a) showed a reversible redox couple at +0.92 V (for the reduction peak) which corresponds to the couple R_5–O_5 during the oxidation of **11** at the potential of the second charge transfer (Figure 2) and a second irreversible peak at +1.25 V. Thus, O_5 and O_6 may be assigned to the two consecutive one-electron transfers for oxidation of **13**. The cyclic voltammogram for the oxidation of **12** (Figure 3b) showed the presence of two reversible one-electron redox couples at +1.15 and +1.28 V (for the reduction peaks) which correspond to the potential of R_4 and R_2 (Figure 2). The steady-state cyclic voltammogram of **11** with a switching potential midway between O_1 and O_3 revealed the presence of a shoulder on O_1 which could be matched with the oxidation peak O_4 of the dimer, **12**. Thus, the voltammetry of **11** is consistent with the formation of **12** at O_1 and the formation of **13** when the potential is stepped far enough anodic to form the dication of **11**.

Effect of Electrolyte, Water Content, Acid, and Base on the Degree of Intramolecular Cyclization of 3,3′-Dimethoxybibenzyl. The form of the cyclic voltammogram for the intramolecular coupling of **5** suggested that cyclic voltammetry could be used for the qualitative estimation of the effect of conditions on the extent of coupling. The height of the cyclized cation radical reduction peak (R_2, Figure 1) was used as a measure of the extent of coupling under varying conditions of nature of the electrolyte, amount of water present, the presence of added acid, and the presence of added base. The cyclization reaction appears to be catalyzed by a combination of acid and water.

Discussion

Attention has recently been called to the fact that perhaps the factor which most seriously limits the utility of oxidative coupling reactions is that in general the dimeric products are more easily oxidized than the substrates.[5,10] In rare cases this difficulty may be overcome by insolubility of the dimeric product in the reaction medium as was encountered during the anodic oxidation of 10-methylene-9-anthrone in acetonitrile.[11] However, in general, overoxidation cannot be avoided and if the synthesis is to be successful, the oxidized form of the dimer must be stable in the medium employed. The use of dichloromethane–TFA mixtures as solvent for the anodic coupling of simple aryl ethers has been successful due to the stability of the cation radicals of the resulting biphenyls in that medium.[5,10]

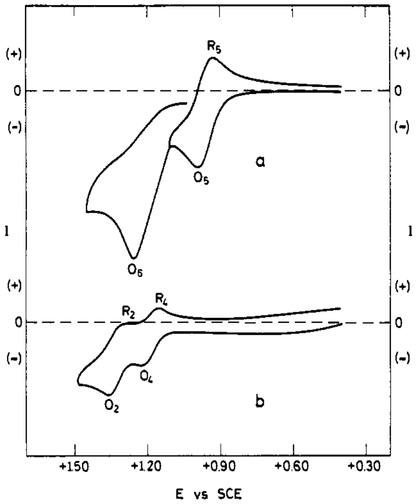

Figure 3. Cyclic voltammograms of the intramolecular (**13**) and intermolecular (**12**) coupling products of 3,3′,4-trimethoxybibenzyl in acetonitrile containing sodium perchlorate (0.1 *M*). Voltage sweep rate 86 mV/sec.

In the case of the oxidative intramolecular coupling reactions of methoxybibenzyls, the oxidized forms of the cyclized products are somewhat stable even in acetonitrile and thus, on the voltammetric time scale the latter solvent is suitable for the observation of the product redox couple, dihydrophenanthrene–cation radical. The latter is clearly demonstrated by the cyclic voltammogram of **2** in acetonitrile (Figure 1). In this case, as well as for the other bibenzyls studied, the cyclic voltammetry is as well defined in acetonitrile as in dichloromethane–TFA. Very different results were obtained with the simple aryl ethers,[5,10] in which case coupled products could not be observed by cyclic voltammetry in acetonitrile.

While acetonitrile proved to be a suitable solvent for voltammetric studies of the anodic cyclization of the bibenzyls, it was found to be totally unsuitable for the preparation of the 9,10-dihydrophenanthrenes. Only trace amounts of the desired products along with major amounts of intractable tars were obtained. This contrasting behavior of voltammetric and preparative experiments is a consequence of the differing time scales of the two types of experiments. The finite lifetimes of the cation radicals of the 9,10-dihydrophenanthrenes produced during the oxidation of the corresponding bibenzyls is sufficient for detection by cyclic voltammetry which only requires lifetimes of the order of seconds. However, preparative experiments require that lifetimes be more of the order of several minutes or longer if the intermediates are to survive. The enhanced stability of aromatic cations in media containing TFA[12,13] provides the stability "boost" necessary to allow high yield anodic cyclization to be carried out on all the methoxybibenzyls as well as the diphenylmethane (**8**).

It is evident from the data in Table I that oxidation

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(10) A. Ronlán, K. Bechgaard, and V. D. Parker, submitted for publication.

(11) V. D. Parker and L. Eberson, *Tetrahedron Lett.*, 1762 (1972).

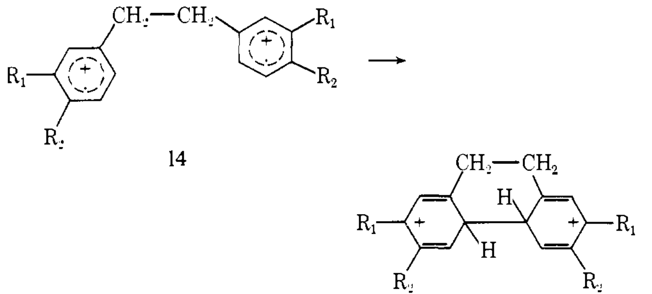
(12) O. Hammerich, N. S. Moe, and V. D. Parker, *J. Chem. Soc., Chem. Commun.*, 156 (1972).

(13) U. Svanholm and V. D. Parker, *Tetrahedron Lett.*, 471 (1972).

of both substrates and cyclized products occurs from 100 to 300 mV more readily in acetonitrile than in the mixed solvent. A similar observation was made for a large group of methoxy-substituted biphenyls and related compounds and was attributed to greater solvation energies of the corresponding cation radicals in the more polar acetonitrile.[14]

In the past, coupling reactions at the anode have generally been attributed to the formation of radical species in close proximity at the electrode surface which dimerize. The most thoroughly studied class of compounds which are especially prone to dimerize are the aromatic amines, and cation radical coupling has been postulated as the mechanism for these reactions.[15] More recently, a mechanism has been proposed for the coupling of aromatic hydrocarbons which involves the attack of anodically generated cation radicals on the aromatic substrate.[6] Since aromatic amines and methoxy aromatic compounds are far more nucleophilic than hydrocarbons, the latter mechanism would appear to be even more plausible for these substrates. However, no clear-cut evidence was available at the outset of the present study which could be used to differentiate between the two mechanisms. The following discussion gives the approach used in the present work to distinguish between the two mechanisms.

The isolation of two aromatic rings by a $-CH_2CH_2-$ group would be expected to have the effect of allowing the two moieties to behave independently with oxidation occurring in one or both of the rings at potentials depending upon the degree and nature of substitution in the rings. Thus, the symmetrically substituted bibenzyls, **2** and **5**, would be expected to undergo two-electron oxidations or very closely spaced consecutive one-electron oxidation steps to produce the dication diradicals of type **14**, which react to give **15**.



This being the case, a cation radical coupling mechanism is imposed upon these substrates for the cyclization to the corresponding 9,10-dihydrophenanthrene. In fact, the oxidations of **2** and **5** do appear as two-electron steps inseparable by the techniques available as illustrated by the peak (O_1) for oxidation of **2** in acetonitrile (Figure 1). The oxidation peak for **2** with two methoxy groups in each ring appears at +1.23 V in acetonitrile while that for **5** with only one methoxy group in each ring appears at +1.62 V. If we accept the argument that isolation of the two rings by the saturated group causes the two rings to behave independently according to the substitution on the rings, then we would predict that **11** should undergo two discrete one-electron oxidation steps first producing the cation radical at about +1.23 V and then the dication diradical at about +1.62 V. A complicating factor arises in this case; if cyclization is to occur at the potential of the first electron transfer, then the electrophilic attack of the cation radical portion of the molecule on the unoxidized part will be imposed upon the reaction. However, if the latter mechanism is not favorable, coupling of cation radicals in an intermolecular reaction is still possible. If reaction occurs at the potential of the first electron transfer, the second electron transfer will not be clearly defined by cyclic voltammetry. Potential step cyclic voltammetry,[8,9] along with product identification proved to be a very penetrating probe of the mechanism of oxidation of **11**. Potential step on the first peak followed by a cathodic sweep (Figure 2) revealed the formation of a product which was reduced at a potential very close to where **11** is oxidized. Low-temperature anodic oxidation of **11** under coulometric conditions resulted in the formation of a compound which showed the same voltammetric peaks as observed during potential step experiments on the first peak. Preparative oxidation of **11** at very low current density resulted in the isolation of the dimer (**12**) in about 50% yield. Voltammetry of **12** matched that from the coulometric product. Thus, it is clear that intermolecular coupling of cation radicals of **11** occurs when the oxidation is carried out at a potential where the monocation is generated even though cyclization by intramolecular attack of the cationic portion of the molecule on the unoxidized part has the advantage of the favorable close proximity of reacting moieties. Potential step to more anodic potentials (Figure 2) gave voltammetry more consistent with that of **2** and **5** with the redox couple due to the oxidation product appearing at more cathodic potentials as expected for the 9,10-dihydrophenanthrene system. The latter couple was identified as indeed being due to **13** and the corresponding cation radical by comparison of the voltammetry of the authentic compound prepared independently by Ullman coupling of the corresponding diiodo compound. Thus, at potentials where the dication diradical is generated, intramolecular cation radical pairing occurs exclusively showing that the intramolecular reaction path is favored over the intermolecular pathway. Therefore, the observation of the dimer (**12**) at low potentials is not due to unfavorable geometry leading to the dihydrophenanthrene.

The experiments with **11** lead to the conclusion that the favored mechanism for anodic coupling of methoxy aromatic compounds is the cation radical dimerization pathway. By analogy, it seems reasonable to postulate that this mechanism should also hold for the anodic coupling of aromatic amines or aromatic hydrocarbons. However, similar evidence to that presented for the methoxy aromatics would be desirable before definitive mechanistic conclusions are drawn for the latter two systems.

One might expect that the coupling of cation radicals be essentially a "no mechanism" reaction with the two entities coming together with only a small activation energy due to repulsive forces of the like charges. Repulsion of the two cationic centers for one another is certainly not prohibitive toward dimerization since it is now known that a variety of cation radicals

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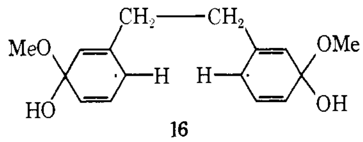
such as those from aromatic hydrocarbons,[16] aromatic amines,[17] and heteroaromatic compounds[18,19] undergo rapid and reversible dimer formation. Thus, there appears to be little or no barrier to formation of cation radical dimers. However, the data strongly suggest that the intramolecular coupling of dication diradicals of methoxybibenzyls is a catalyzed process. A possible explanation of the catalytic effect is that association of water with the cationic portions of the molecule localizes the free electron in a position favorable for dimerization to occur. An extreme structure for this effect would be hemiketal formation (**16**).



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The function of acid could then be as a catalyst for hemiketal formation.

Experimental Section

General procedures, purification of solvents, and apparatus used for voltammetry and coulometry were conventional and described in previous papers.[20,21]

3,3′,4,4′-Tetramethoxybibenzyl (2) was prepared from the corresponding stilbene[22,23] by catalytic (10% Pd on carbon) hydrogenation at atmospheric pressure in 95% ethanol, mp 109–110° (lit.[24] mp 109–110°).

3,3′-Dimethoxybibenzyl (5) was prepared from the corresponding stilbene[22,25] by the same method as 3,3′,4,4′-tetramethoxybibenzyl, mp 39.5–40.5° (lit.[26] mp 39–40°).

Bis(3-methoxyphenyl)methane (8) was prepared as described in the literature,[27] bp 197–198° (8 mm) (lit.[27] bp 196–198°).

2,3,6,7-Tetramethoxy-9,10-dihydrophenanthrene (3) was prepared from 3,3′,4,4′-tetramethoxybibenzyl as described in the literature,[24] mp 174–175° (lit.[24] mp 174–175.5°).

2,7-Dimethory-9,10-dihydrophenanthrene (6) was prepared from 3,3′-dimethoxybibenzyl by the same route as the tetramethoxy analog, mp 108–109° (lit.[28] mp 108–109°).

2,7-Dimethoxyfluorene (9) was prepared by Ullman coupling of bis(2-iodo-5-methoxyphenyl)methane:[29] mp 168–168.5°; nmr ($CDCl_3$) δ 3.86 (s, 6 H), 7.03 (m, 4 H), 7.63 (d, J = 8 Hz, 2 H). *Anal.* Calcd for $C_{15}H_{14}O_2$: C, 79.6; H, 6.3; M^+, 226. Found: C, 79.7; H, 6.2; M^+, 226.

2,3,6,7-Tetramethoxyphenanthrene (4) was prepared from 3,3′,4,4′-tetramethoxystilbene by irradiation in absolute ethanol in presence in iodine.[30] The photolysis yielded a mixture of isomeric phenanthrenes from which the product could be isolated by fractionated crystallization from toluene–hexane (1:1), yield 52%, mp 180–181° (lit.[31] mp 178°).

3,3′,4-Trimethoxybibenzyl (11) was prepared by hydrogenation of 3,3′,4-trimethoxystilbene[32] in ethanol over a palladium on carbon (10%) catalyst. The crude product was purified by chromatography on silica gel (eluent, benzene): mp 34–36°; nmr ($CDCl_3$) δ 2.83 (s, 4 H), 3.67 (s, 3 H), 3.77 (s, 6 H), 7 (m, 7 H). *Anal.* Calcd for $C_{17}H_{20}O_3$: C, 75.0; H, 7.4; M^+, 272. Found: C, 75.0; H, 7.6; M^+, 272.

2,3,7-Trimethoxy-9,10-dihydrophenanthrene (13). Copper powder (30 g) and 2,2′-diiodo-3,3′,4-trimethoxybibenzyl[33] (10 g) were mixed intimately and heated to 300° in a flask fitted with an air cooled condenser. After 15 min the condenser was connected to a vacuum pump (0.1 mm) and the product (5 g of a yellow oil) distilled from the reaction flask into the condenser. The oil was dissolved in hot ethanol (25 ml) and upon standing crystals (2.5 g) separated. Recrystallization from ethanol yielded pure 2,3,7-trimethoxy-9,10-dihydrophenanthrene (2 g): mp 100–101°; nmr ($CDCl_3$) δ 2.78 (s, 4 H), 3.80 (s, 3 H), 3.87 (s, 3 H), 3.91 (s, 3 H), 6.77 (m, 3 H), 7.22 (s, 1 H), 7.57 (d, J = 9 Hz, 1 H). *Anal.* Calcd for $C_{17}H_{18}O_3$: C, 75.6; H, 6.7; M^+, 270. Found: C, 75.8; H, 6.6; M^+, 270. Evaporation of the mother liquors and chromatography of the residue on silica gel (400 g) with benzene as eluent yielded 3,3′,4-trimethoxybibenzyl (1.8 g), 2,3,7-trimethoxy-9,10-dihydrophenanthrene (0.6 g), and a new compound (0.4 g): mp 104–105°; nmr ($CDCl_3$) δ 3.83 (s, 3 H), 3.90 (s, 3 H), 3.97 (s, 3 H), 7.05 (m, 3 H), 7.45 (s, 2 H), 7.74 (s, 1 H), 8.29 (d, J = 10 Hz, 1 H). From these data the new compound was identified as 2,3,7-trimethoxyphenanthrene. *Anal.* Calcd for $C_{17}H_{16}O_3$: C, 76.1; H, 6.0; M^+, 268. Found: C, 76.1; H, 5.9; M^+, 268.

Preparative Electrolysis, General. The compound to be oxidized (2 mmol) was dissolved in dichloromethane–TFA (4:1, 100 ml) or acetonitrile (100 ml) containing tetrabutylammonium fluoroborate (0.1 *M*). This solution was subjected to constant current (200 mA) electrolysis on a platinum anode (75 cm²) under nitrogen in a closed two compartment cell. The anode compartment was separated from the cathode compartment by a glass fritt (G4, 30 mm diameter). The cathode was a platinum wire. The cell content was stirred magnetically and kept at 8° by external cooling. If a colored solution was obtained after the calculated amount of current had been passed through the electrolysis solution the polarity of the cell was reversed and the electrolysis continued until the content of the former anode compartment turned colorless. The same results were obtained if zinc powder was used as the reducing agent. The contents of the anode and the cathode compartment were combined and evaporated *in vacuo* (10 mm) at 40°. The residue was treated with dry ether (3 × 75 ml) to precipitate the supporting electrolyte. The combined ether extracts were evaporated *in vacuo* and the residue was chromatographed on a 2.5 × 80 cm silica acid column slurry packed in 50% ether–hexane and eluted with 1600 ml of 50% ether–hexane (25-ml fractions).

Anodic Oxidation of 3,3′,4,4′-Tetramethoxybibenzyl (2). (a) In Acetonitrile. The compound (2 mmol, 604 mg) was oxidized as described above. Current corresponding to 4 F/mol was passed through the cell. The current was not reversed but the resulting dark-brown solution was worked up as described above yielding starting material (280 mg) and 2,3,6,7-tetramethoxyphenanthrene (**4**) (60 mg) (identified by comparison with an authentic sample prepared as described above). During the electrolysis a bluish-black polymeric film (198 mg) was formed on the anode.

(b) In Dichloromethane–TFA (4:1). The electrolysis was carried out exactly as the oxidation in acetonitrile yielding starting material (24 mg) and 2,3,6,7-tetramethoxyphenanthrene (588 mg).

Anodic Oxidation of 2,3,6,7-Tetramethoxy-9,10-dihydrophenanthrene (3). (a) In Acetonitrile. The compound (2 mmol, 600 mg) was oxidized as described above. Current corresponding to 2 F/mol was passed through the cell. The current was not reversed but the resulting dark-brown solution was worked up as described

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(32) Prepared from 3-methoxybenzaldehyde and 3,4-dimethoxybenzyl chloride: mp 145–146°; nmr ($CDCl_3$) δ 3.82 (s, 3 H), 3.85 (s, 3 H), 3.88 (s, 3 H), 7 (m, 9 H). *Anal.* Calcd for $C_{17}H_{18}O_3$: C, 75.6; H, 6.7; M^+, 270. Found: C, 75.4; H, 6.7; M^+, 270.

(33) Prepared by stirring 3,3′,4-trimethoxybibenzyl (20 g) with iodine monochloride (23.6 g) in glacial acetic acid (150 ml) for 72 hr: mp 104–105° (acetic acid); nmr ($CDCl_3$) δ 2.93 (s, 4 H), 3.73 (s, 3 H), 3.77 (s, 3 H), 3.83 (s, 3 H), 6.67 (m, 3 H), 7.23 (s, 1 H), 7.70 (d, J = 8 Hz, 1 H). *Anal.* Calcd for $C_{17}H_{18}I_2O_3$: I, 48.6. Found: I, 48.5.

above yielding starting material (18 mg) and 2,3,6,7-tetramethoxyphenanthrene (560 mg).

(b) In Dichloromethane–TFA (4:1). The electrolysis was carried out exactly as in acetonitrile yielding starting material (19 mg) and 2,3,6,7-tetramethoxyphenanthrene (557 mg).

Anodic Oxidation of 3,3′-Dimethoxybibenzyl (5). (a) In Acetonitrile. The compound (2 mmol, 484 mg) was oxidized as described above. Current corresponding to 3 F/mol was passed through the cell. The current was not reversed but the resulting dark-brown solution was worked up directly yielding only starting material (484 mg) and tars.

(b) In Dichloromethane–TFA (4:1). The electrolysis was carried out as in acetonitrile. The resulting solution was intensely green. Reversal of the current rendered the solution dark-brown after the passage of an amount of current corresponding to 0.8 F/mol. Work-up in the usual manner yielded starting material (16 mg) and 2,7-dimethoxy-9,10-dihydrophenanthrene (449 mg).

Anodic Oxidation of Bis(3-methoxyphenyl)methane (8). (a) In Acetonitrile with Tetrabutylammonium Fluoroborate as Supporting Electrolyte. The compound (2 mmol, 456 mg) was oxidized as described above. Current corresponding to 3 F/mol was passed through the cell. The current was not reversed but the resulting dark-brown solution was worked up directly yielding starting material (290 mg), 3,7-dimethoxyfluorene (60 mg), and polymers (50 mg).

(b) In Acetonitrile with Lithium Perchlorate (0.1 *M*) as Supporting Electrolyte. Current corresponding to 3 F/mol was passed through the cell. During the electrolysis a black precipitate was formed in the solution and on the anode surface. The precipitate dissolved in acetonitrile with an intense blue color and in nitromethane with an intense green color. Both solutions gave strong esr signals. The black precipitate was reduced with zinc powder in the electrolysis solution and after filtration work-up of the filtrate was continued in the usual manner yielding starting material (120 mg), 3,7-dimethoxyfluorene (180 mg), and polymers (95 mg).

(c) In Dichloromethane–TFA (4:1). The compound (2 mmol, 456 mg) was oxidized as described above. Current corresponding to 3 F/mol was passed through the cell. Reversal of the current rendered the solution colorless after the passage of an amount of current corresponding to 0.7 F/mol. Work-up in the usual manner yielded starting material (90 mg) and 3,7-dimethoxyfluorene (316 mg).

Anodic Oxidation of 3,3′,4-Trimethoxybibenzyl (11). (a) The compound (816 mg, 3 mmol) was dissolved in CH_2Cl_2–TFA (4:1, 150 ml) containing *n*-Bu_4NBF_4 (0.1 *M*) and under N_2 subjected to constant current (current density 3×10^{-5} A/cm^2) electrolysis in a divided cell at −25°. When an amount of current corresponding to 2 F/mol had been passed through the cell, the electrolysis was interrupted and zinc powder (2 g) and water (50 ml) were added to the anolyte. After 2 min of stirring the color of the anolyte had changed from blue to yellow and the mixture was filtered. The organic phase was washed with a saturated bicarbonate solution (50 ml) and water (50 ml), dried over sodium sulfate, and evaporated. The resulting oil was chromatographed on 100 g of silica gel (benzene–ether 5:1) yielding starting material (208 mg) and a new compound (375 mg): mp 98–99°; nmr ($CDCl_3$) δ 2.67 (s, 8 H), 3.67 (s, 6 H), 3.83 (s, 6 H), 3.88 (s, 6 H), 6.50–7.33 (m, 12 H); *m/e* 542 (M^-). On the basis of these data structure **12** was assigned to the new compound. *Anal.* Calcd for $C_{34}H_{38}O_6$: C, 75.2; H, 7.0. Found: C, 75.4; H, 6.8.

(b) A similar experiment as under (a) was carried out with a current density of 1×10^{-1} A/cm^2. An amount of current corresponding to 6 F/mol was passed through the cell. Chromatography on silica gel yielded starting material (315 mg), **12** (96.5 mg), and 2,3,7-trimethoxyphenanthrene (11 mg) identified by comparison with an authentic sample.

Anodic Oxidation of 2,3,7-Trimethoxy-9,10-dihydrophenanthrene (13) in Dichloromethane–TFA (4:1). The compound (2 mmol, 540 mg) was oxidized as described above. Current corresponding to 2 F/mol was passed through the cell. The resulting green solution was rendered colorless by addition of zinc powder. Work-up in the usual manner yielded 2,3,7-trimethoxyphenanthrene (299 mg) and 2,3,7-trimethoxy-9,10-dihydrophenanthrene (13 mg).

Catalysis of the β-Elimination of *O*-Phosphothreonine by Pyridoxal and Metal Ions[1]

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Abstract: The β-elimination reaction of *O*-phosphothreonine was investigated in aqueous media at 45.0 ± 0.1° in the presence of pyridoxal and various metal ions. Of the six metal ions employed only copper(II) and oxovanadium(IV) ions have strong catalytic effects. In the pyridoxal–copper(II) catalysis the rate increased as pH was raised from neutrality with a rate plateau being observed in the region of pH 8–10. For the pyridoxal–vanadyl(IV) catalysis the rate maximum was reached in the region of $-\log [H^+] \simeq 5.5$. On the basis of equilibrium studies of the pyridoxal–metal–threonine and related systems by means of electronic spectroscopy, the observed catalysis was ascribed to the formation of metal complexes of the amino acid–pyridoxal Schiff base having a 1:1 molar ratio of ligand to metal ion. The addition of organic bases (*i.e.*, piperidine and morpholine) resulted in further rate enhancement. This catalysis was attributed to a rate-determining step involving combination of the base with a proton abstracted from the α position of the amino acid, and the concomitant liberation of the phosphate group by carbon–oxygen fission. The catalytic activity observed in these systems seem to be derived from the electronic effect of metal ions in the Schiff base complexes in a direction which promotes hydrogen abstraction. A reaction mechanism for metal ion–pyridoxal catalysis of elimination of phosphate groups substituted in the β position of amino acids is proposed.

Among various nonenzymatic reactions of α-amino acids, β-elimination reactions were observed to occur with appropriate β-substituted amino acids in the presence of pyridoxal and metal ions. The substrates include serine,[2a] threonine,[2b] β-chloroalanine,[3]

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