

Anodic Cyanation of *tert*-Butylated Anisoles: Competitive Aromatic Additions and Substitutions

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The electrooxidation of several *tert*-butylated anisoles has been carried out in methanol containing sodium cyanide at a Pt anode in a divided cell. Two types of reactions occurred competitively, aromatic-ring addition and substitution. Increasing the level of *tert*-butyl substitution raises the relative extent of addition to the aromatic ring. An MO calculation has indicated that the order of orientational preference for substitution of the aromatic hydrogen of alkylanisole cation radicals is explained in terms of the LUMO electron densities calculated for the cation radicals. The effect of structure on the oxidation potential of alkylanisoles has also been studied. *para* Substitution lowers the oxidation potential while *ortho* substitution raises the potential.

Many of the electrooxidations of alkylated aromatic compounds are considered to proceed by way of monocation radical intermediates and it is common to observe products resulting from substitution on both the aliphatic side-chain and the aromatic nucleus.¹ Previously, we have reported a study of the electrooxidation of the three isomeric methylanisoles in methanol containing sodium cyanide.² With *ortho*- and *meta*-methylated anisoles, nuclear cyanation took place preferentially while with *p*-methylanisole, side-chain methoxylation predominated. The data obtained was also compared with those of other electron-transfer reactions such as anodic acetoxylation and acetoxylation and chlorination by metal oxidizing agents. It has been shown that positional reactivities are rationalized in terms of the LUMO electron densities calculated for the cation radicals.³

As part of our programme of electrochemical functionalization of alkylated aromatic compounds, the present paper describes the electrooxidation of several *tert*-butylated anisoles in methanol containing sodium cyanide. Not only does the *tert*-butyl substituent lack α proton but, like a methyl group, it releases electrons and activates the ring.

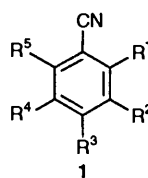
Results

Oxidation Potentials.—Cyclic voltammograms were recorded for a series of *tert*-butyl-substituted anisoles using a solution of 0.4 mol dm⁻³ NaCN in methanol. The reference electrode was an SCE (saturated calomel electrode). The background current with this system began to increase at potentials more anodic than 1.60 V. The observed E_p values are collected in Table 1.

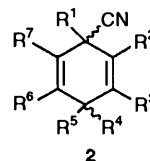
Products.—The oxidations, carried out at a constant current of 0.1 A in a divided cell with a Pt anode, at room temperature, were terminated after passage of 2.0 F mol⁻¹ of added substrate. After work-up, the products were isolated by preparative GLC and identified by elemental analysis and ¹H NMR, IR and mass spectroscopic analyses (Table 2).

Initially we studied *tert*-butylbenzene (TBB). All three possible isomeric *tert*-butylbenzonitriles were produced in a total yield of 3% (based on unrecovered starting material), the conversion being 15%. Most of the current would be consumed in oxidation of the cyanide ion, an inorganic electrode process not producing isolable cyanated products.

tert-Butylanisoles (TBAs) undergo predominantly two types of aromatic-cyanation reactions: (1) substitution of aromatic



- 1
- a R¹ = Bu^t, R² = R³ = R⁴ = R⁵ = H
 b R² = Bu^t, R¹ = R³ = R⁴ = R⁵ = H
 c R³ = Bu^t, R¹ = R² = R⁴ = R⁵ = H
 d R¹ = OMe, R² = R³ = R⁴ = R⁵ = H
 e R³ = OMe, R¹ = R² = R⁴ = R⁵ = H
 f R² = Bu^t, R³ = OMe, R¹ = R⁴ = R⁵ = H
 g R¹ = OMe, R² = Bu^t, R³ = R⁴ = R⁵ = H
 h R¹ = R³ = Bu^t, R² = R⁴ = R⁵ = H
 i R¹ = OMe, R⁴ = Bu^t, R² = R³ = R⁵ = H
 j R¹ = R⁵ = Bu^t, R² = R³ = R⁴ = H
 k R¹ = R³ = Bu^t, R⁴ = OMe, R² = R⁵ = H
 l R¹ = OMe, R² = R⁴ = Bu^t, R³ = R⁵ = H
 m R¹ = R³ = R⁵ = Bu^t, R² = H
 n R² = R⁴ = Bu^t, R³ = OMe, R¹ = R⁵ = H
 o R¹ = R³ = Bu^t, R² = OMe, R⁴ = R⁵ = H
 p R¹ = R⁵ = Bu^t, R³ = OMe



- 2
- a R¹ = OMe, R⁴ = CN, R⁵ = Bu^t, R² = R³ = R⁶ = R⁷ = H
 b R¹ = R⁴ = OMe, R² = R⁵ = Bu^t, R³ = R⁶ = R⁷ = H
 c R¹ = OMe, R² = R⁵ = Bu^t, R⁴ = CN, R³ = R⁶ = R⁷ = H
 d R¹ = R⁴ = OMe, R² = R⁵ = R⁷ = Bu^t, R³ = R⁶ = H
 e R¹ = OMe, R² = R⁵ = R⁷ = Bu^t, R³ = R⁶ = H
 f R¹ = R⁴ = OMe, R² = R⁷ = Bu^t, R³ = R⁵ = R⁶ = H
 g R¹ = R³ = R⁶ = Bu^t, R² = OMe, R⁴ = CN, R⁵ = R⁷ = H

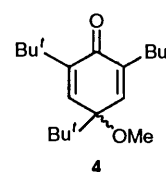
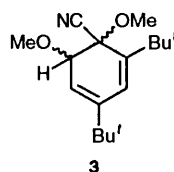


Table 1 Products and yields of electrooxidation of *tert*-butylated anisoles in NaCN–MeOH^a

Substrate	E_p (V vs. SCE) ^b	Conversion (%)	Product	Yield (%) ⁱ
TBB	— ^c	15	1a	1.5
			1b	0.5
			1c	1
2-TBA	1.71	89	1f	36
			1g	23
			1a	20
			1d	3
4-TBA	1.57	91	1i	37
			1c	26
			1e	4
2,4-DTBA	1.47	94	2a	<i>j</i>
			1h	22
			1l	17
			1f	6
			1k	1
			2b^d	14
2,6-DTBA	— ^c	43	2c^e	9
			3	2
			1n	41
			1j	12
			1o	10
			1g	9
			1p	10
2,4,6-TTBA	~ 1.8	69	2f^f	17
			2d^g	40
			2e^h	7
			2g	1.5
			4	3
			1m	8
			1l	4
			1n	4

^a Constant-current electrooxidation at 0.1 A. Pt anode; divided cell; electricity 2.0 F mol⁻¹; substrate concentration 0.4 mol dm⁻³. ^b 0.4 mol dm⁻³ NaCN–MeOH; at v 0.1 V s⁻¹. ^c In these cases the oxidation wave was not observed due to the large background current from the concurrent electrooxidation of the solvent–electrolyte system. ^d 24% *cis*, 76% *trans*. ^e 50% *cis*, 50% *trans*. ^f 12% *cis*, 88% *trans*. ^g 35% *cis*, 65% *trans*. ^h 47% *cis*, 53% *trans*. ⁱ Based on unrecovered starting material. ^j < 0.5% yield.

hydrogen and (2) replacement of an aromatic methoxy group. 2-TBA gave hydrogen-displacement products, 3-*tert*-butyl-4-methoxybenzotrile **1f** (36%) and 3-*tert*-butyl-2-methoxybenzotrile **1g** (23%), together with the methoxy-displacement product, 2-*tert*-butylbenzotrile **1a** (20%). 4-TBA afforded 5-*tert*-butyl-2-methoxybenzotrile **1i** (37%) and 4-*tert*-butylbenzotrile **1c** (26%), along with a small amount of 1,4-dicyano adduct **2a**. In both cases, *tert*-butyl displacement occurred, although this is a minor pathway.

Cyanation of di-*tert*-butylanisoles (DTBAs) occurred at their methoxy and/or *tert*-butyl groups as well as by replacement of aromatic hydrogen, 1,4 addition of cyano and/or methoxy group(s) competing with aromatic substitution. Besides these, 2,4-DTBA underwent the 1,2-mixed addition of one cyano and one methoxy group with the formation of a small amount of 2,4-di-*tert*-butyl-1,6-dimethoxycyclohexa-2,4-diene-1-carbonitrile **3**. 2,6-DTBA gave an abnormal hydrogen-displacement product, 2,6-di-*tert*-butyl-4-methoxybenzotrile **1p** (10%), produced by elimination of a methanol molecule from the 1,4-mixed addition product, 1,4-dimethoxy-2,6-di-*tert*-butylcyclohexa-2,5-diene-1-carbonitrile **2f**, during GLC analysis.

With 2,4,6-tri-*tert*-butylanisole (2,4,6-TTBA), the reaction mode was reversed and addition predominated over substitution. At the 3 position, there was no substitution of the aromatic-hydrogen but 1,4-addition of two cyano groups across the benzene ring occurred with formation of the adduct **2g**.

Compound **4** is a secondary product of 1,3,5-tri-*tert*-butyl-3,6,6-trimethoxycyclohexa-1,4-diene upon hydrolytic work-up.

Structure Determination.—The result of previous ¹H NMR spectroscopic studies on geometrical isomerism in 2,5-dihydrofurans,^{10,11} 2,5-dihydrothiophenes^{12,13} and 2,3-dihydrobenzothiophenes¹⁴ were applicable to structural assignments of isomeric pairs of the relevant cyclohexadienes **2**. The chemical shift of a group in the 1 position of the cyclohexadiene ring is affected both by the other group at the 1 position and the magnetic influence exerted by the group at the 4 position that is *cis* to it. Thus, if a 1-methoxy group is *cis* to a 4-methoxy (or a 4-cyano) group it will resonate at a lower field and raise the δ value compared with the values obtained if it is *cis* to a 4-*tert*-butyl (or a 4-protium) group.

The structure assigned to **2g** was based on its spectroscopic characteristics. The C₂₁H₃₂N₂O molecular formula was indicated by mass spectroscopy and verified by elemental analysis. The IR spectrum indicated the presence of a cyano group. The NMR spectrum showed three *tert*-butyl resonances at 1.25 (9 H, s), 1.30 (9 H, s) and 1.34 (9 H, s), a doublet at 3.36 (1 H, methine bonded to a cyano group), one methoxy resonance at 3.54 (3 H, s) and one olefinic proton at 5.80 (1 H, d).

The structural assignment to compound **3** was also supported by its combustion analysis and mass, IR and NMR spectra. NMR spectroscopy (δ in CDCl₃) showed two *tert*-butyl resonances at 1.10 (9 H, s) and 1.28 (9 H, s), two methoxy protons at 3.34 (3 H, s) and 3.60 (3 H, s), one doublet at 4.10 (1 H, methine bonded to a methoxy group) and two olefinic protons at 5.74 (1 H, dd) and 6.10 (1 H, d).

Discussion

The cyanation of several *tert*-butylated anisoles has been investigated. Two types of reactions are observed: aromatic ring substitution is favoured for anisoles having a *tert*-butyl substituent on either the *ortho* or *para* (or both) position(s) and nuclear addition for compounds having the *tert*-butyl substituent on all *ortho* and *para* positions. With increasing numbers of *tert*-butyl groups the relative extent of addition to the benzene ring is raised. Heretofore, anodic 1,4-addition of one cyano and one methoxy groups across the benzene ring has been reported for 1,4-dimethoxybenzene.¹⁵ 1,4,4-Trimethoxycyclohexa-2,5-diene-1-carbonitrile was isolated although it contained an impurity difficult to separate.

The Effect of Structure on Oxidation Potential.—The oxidation wave of the parent anisole was not observed since it was masked by the large background current from the concurrent electrooxidation of the solvent–electrolyte system. The potentials depend upon the number and position(s) of the substituent. As can be seen from Table 1, *para* substitution lowers the oxidation potential while *ortho* (markedly di-*ortho*) substitution, where steric effects can prevail, raises the potential. For comparison, E_p s for *ortho*-methyl- and *para*-methyl-anisole were measured (1.75 and 1.55 V vs. SCE at v 0.1 V s⁻¹, respectively) and compared with those of the corresponding *tert*-butylated anisoles. It was ascertained that there is little difference in the substituent effects between *tert*-butyl and methyl groups. A similar substituent effect appears in the conversion of substrates in the present electroreaction. The results are shown in Table 1.

Orientation.—Both addition and substitution on the benzene ring are formally a 2-equiv. change. The cyclic voltammetric characteristics indicate that oxidation is initiated by electron transfer from the substrate molecule, followed by a fast chemical reaction. By analogy with anodic cyanation and related func-

Table 2 Spectroscopic data of electrooxidation products

Product	¹ H NMR [δ (J/Hz)] ^{bb}	Mass <i>m/z</i> (M ⁺)	IR (ν_{\max} /cm ⁻¹) ^{dd}
1a ^a	1.52 (9 H, s), 7.14–7.72 (4 H, m)	159	2220 (CN)
1b ^b	1.32 (9 H, s), 7.30–7.50 (2 H, m), 7.50–7.66 (2 H, m)	159	2220 (CN)
1c ^c	1.32 (9 H, s), 7.36–7.64 (4 H, m)	159	2220 (CN)
1d	1.37 (9 H, s), 3.82 (3 H, s), 6.70–6.95 (2 H, m), 7.02–7.32 (2 H, m)		
1e	1.28 (9 H, s), 3.78 (3 H, s), 6.81 (2 H, dm, <i>J</i> 8.6), 7.27 (2 H, dm, <i>J</i> 8.6)		
1f ^d	1.36 (9 H, s), 3.88 (3 H, s), 6.80–6.92 (1 H, m), 7.38–7.54 (2 H, m)	189	1025, 1095 (C–O–C), 2210 (CN)
1g ^e	1.36 (9 H, s), 4.12 (3 H, s), 6.9–7.1 (1 H, m), 7.3–7.6 (2 H, m)	189	1000, 1095 (C–O–C), 2210 (CN), 2870 (OMe)
1h ^f	1.31 (9 H, s), 1.51 (9 H, s), 7.1–7.7 (3 H, m)	215	2200 (CN)
1i ^g	1.28 (9 H, s), 3.90 (3 H, s), 6.74–6.92 (1 H, m), 7.4–7.6 (2 H, m)	189	1020, 1105, 1140 (C–O–C), 2220 (CN), 2860 (OMe)
1j ^h	1.54 (18 H, s), 7.3–7.4 (3 H, m)	215	2200 (CN)
1k ⁱ	1.35 (9 H, s), 1.48 (9 H, s), 3.82 (3 H, s), 7.06 (1 H, s), 7.34 (1 H, s)	245	1060, 1115 (C–O–C), 2210 (CN), 2870 (OMe)
1l ^j	1.28 (9 H, s), 1.36 (9 H, s), 4.08 (3 H, s), 7.38 (1 H, d, <i>J</i> 2.3) 7.50 (1 H, d, <i>J</i> 2.3)	245	1000, 1120 (C–O–C), 2210 (CN)
1m ^k	1.32 (9 H, s), 1.56 (18 H, s), 7.34 (2 H, s)	271	2280 (CN)
1n ^l	1.40 (18 H, s), 3.70 (3 H, s), 7.50 (2 H, s)	245	1000, 1120 (C–O–C), 2220 (CN)
1o ^m	1.40 (9 H, s), 1.64 (9 H, s), 3.58 (3 H, s), 7.16 (1 H, d, <i>J</i> 8.1), 7.34 (1 H, d, <i>J</i> 8.1)	245	1020, 1045 (C–O–C), 2210 (CN)
1p ⁿ	1.54 (18 H, s), 3.84 (3 H, s), 6.84 (2 H, s)	245	2210 (CN)
2a-cis	1.12 (9 H, s), 3.36 (3 H, s), 6.0–6.4 (4 H, m)	cc	960, 970, 1055, 1090 (C–O–C), 2210 (CN)
2a-trans	1.10 (9 H, s), 3.46 (3 H, s), 6.20 (4 H, s)	cc	960, 1075 (C–O–C), 2225 (CN)
2b-cis ^o	0.92 (9 H, s), 1.34 (9 H, s), 3.02 (3 H, s), 3.34 (3 H, s), 6.0–6.1 (3 H, m)	277	1075 (C–O–C)
2b-trans ^p	0.92 (9 H, s), 1.34 (9 H, s), 3.00 (3 H, s), 3.30 (3 H, s), 6.06 (1 H, d, <i>J</i> 2.3), 6.12 (1 H, d, <i>J</i> 2.3), 6.14 (1 H, s)	277	1075 (C–O–C), 2820 (OMe)
2c-cis ^q	1.10 (9 H, s), 1.34 (9 H, s), 3.26 (3 H, s), 6.0–6.3 (3 H, m)	272	975, 1020, 1045, 1075, 1090 (C–O–C), 2220 (CN)
2c-trans ^r	1.10 (9 H, s), 1.34 (9 H, s), 3.40 (3 H, s), 6.0–6.3 (3 H, m)	272	955, 975, 1075, 1085 (C–O–C), 2220 (CN)
2d-cis ^s	0.94 (9 H, s), 1.41 (18 H, s), 3.00 (3 H, s), 3.04 (3 H, s), 6.17 (2 H, s)	cc	1075, 1095 (C–O–C), 2220 (CN)
2d-trans ^t	0.96 (9 H, s), 1.41 (18 H, s), 2.94 (3 H, s), 2.96 (3 H, s), 6.16 (2 H, s)	333	1065, 1095 (C–O–C), 2220 (CN), 2820 (OMe)
2e-cis ^u	1.10 (9 H, s), 1.41 (18 H, s), 2.92 (3 H, s), 6.24 (2 H, s)	cc	1065, 1095 (C–O–C), 2225 (CN)
2e-trans ^v	1.12 (9 H, s), 1.41 (18 H, s), 2.93 (3 H, s), 6.24 (2 H, s)	cc	965, 1085 (C–O–C), 2220 (CN)
2f-cis ^w	1.38 (18 H, s), 2.94 (3 H, s), 3.34 (3 H, s), 4.28 (1 H, t, <i>J</i> 3.1), 6.28 (2 H, d, <i>J</i> 3.1)	277	ee
2f-trans ^x	1.38 (18 H, s), 2.84 (3 H, s), 3.16 (3 H, s), 4.45 (1 H, t, <i>J</i> 3.1), 6.28 (2 H, d, <i>J</i> 3.1)	277	1060, 1090 (C–O–C), 2210 (CN), 2825 (OMe)
2g ^y	1.25 (9 H, s), 1.30 (9 H, s), 1.34 (9 H, s), 3.36 (1 H, d, <i>J</i> 0.7), 3.54 (3 H, s), 5.80 (1 H, d, <i>J</i> 0.7)	328	1095, 1135 (C–O–C), 2230 (CN)
3 ^z	1.10 (9 H, s), 1.28 (9 H, s), 3.34 (3 H, s), 3.60 (3 H, s), 4.10 (1 H, d, <i>J</i> 5.1), 5.74 (1 H, dd, <i>J</i> 5.1, 1.4), 6.10 (1 H, d, <i>J</i> 1.4)	277	1100, 1120 (C–O–C), 2210 (CN), 2825 (OMe)
4 ^{aa}	0.94 (9 H, s), 1.25 (18 H, s), 3.14 (3 H, s), 6.51 (2 H, s)	292	1075 (C–O–C), 1640 (C=C), 1660 (C=O), 2850 (OMe)

^a Ref. 4. ^b Ref. 5. ^c Ref. 6. ^d Ref. 7. ^e Found: C, 76.1; H, 7.9; N, 7.7. C₁₂H₁₅NO requires C, 76.2; H, 8.0; N, 7.4%. ^f Found: C, 83.6; H, 9.9; N, 6.6. C₁₅H₂₁N requires C, 83.7; H, 9.8; N, 6.5%. ^g Found: C, 75.7; H, 8.1; N, 7.8. C₁₂H₁₅NO requires C, 76.2; H, 8.0; N, 7.4%. ^h Found: C, 83.7; H, 9.9; N, 6.5. C₁₅H₂₁N requires C, 83.7; H, 9.8; N, 6.5%. ⁱ Found: C, 77.9; H, 9.5; N, 5.8. C₁₆H₂₃NO requires C, 78.3; H, 9.5; N, 5.7%. ^j Found: C, 78.2; H, 9.5; N, 5.7. C₁₆H₂₃NO requires C, 78.3; H, 9.5; N, 5.7%. ^k Ref. 8. ^l Ref. 9. ^m Found: C, 78.1; H, 9.6; N, 5.8. C₁₆H₂₃NO requires C, 78.3; H, 9.5; N, 5.7%. ⁿ This material was isolated containing **2f** as an impurity difficult to separate. ^o Found: C, 73.6; H, 9.8; N, 5.2. C₁₇H₂₇NO₂ requires C, 73.6; H, 9.8; N, 5.1%. ^p Found: C, 73.6; H, 9.7; N, 5.1. C₁₇H₂₇NO₂ requires C, 73.6; H, 9.8; N, 5.1%. ^q Found: C, 75.0; H, 9.0; N, 10.0. C₁₇H₂₄NO₂ requires C, 75.0; H, 8.9; N, 10.3%. ^r Found: C, 74.8; H, 8.9; N, 10.1. C₁₇H₂₄NO₂ requires C, 75.0; H, 8.9; N, 10.3%. ^s Found: C, 75.6; H, 10.2; N, 4.4. C₂₁H₃₅NO₂ requires C, 75.6; H, 10.6; N, 4.2%. ^t Found: C, 75.6; H, 10.2; N, 4.4. C₂₁H₃₅NO₂ requires C, 75.6; H, 10.6; N, 4.2%. ^u Found: C, 76.7; H, 9.6; N, 8.5. C₂₁H₃₂N₂O requires C, 76.8; H, 9.8; N, 8.5%. ^v Found: C, 76.7; H, 9.8; N, 8.5. C₂₁H₃₂N₂O requires C, 76.8; H, 9.8; N, 8.5%. ^w This material was isolated containing **1p** as an impurity difficult to separate. Spectral analyses take this impurity into account. ^x Found: C, 74.0; H, 9.8; N, 5.2. C₁₇H₂₇NO₂ requires C, 73.6; H, 9.8; N, 5.1%. ^y Found: C, 76.5; H, 9.7; N, 8.2. C₂₁H₃₂N₂O requires C, 76.8; H, 9.8; N, 8.5%. ^z Found: C, 73.6; H, 9.8; N, 5.1. C₁₇H₂₇NO₂ requires C, 73.6; H, 9.8; N, 5.1%. ^{aa} Found: C, 77.3; H, 10.8. C₁₉H₃₂O₂ requires C, 78.0; H, 11.0%. ^{bb} 100 MHz; CDCl₃ solution; standard Me₄Si. ^{cc} The parent peak was not observed. ^{dd} Mull for solid sample. ^{ee} The CN stretching vibration of **1p** as impurity masks that of this product.

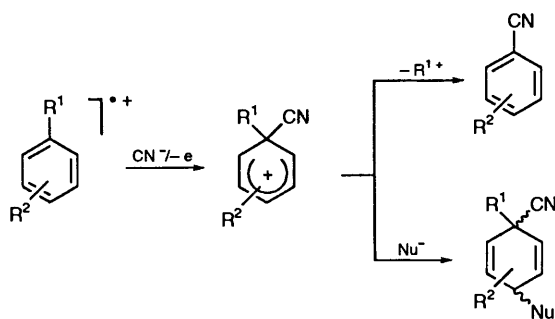
tionalization of other aromatic compounds,¹ the ECEC mechanism involving a cation-radical intermediate would be reasonable.

The generalized mechanism presented in Scheme 1 accounts for anodic bond formation of *tert*-butylated anisoles, where R represents the leaving group such as a hydrogen atom and *tert*-butyl and methoxy groups and Nu is the nucleophile. This mechanism involves two competitive pathways, addition and substitution. The bond-forming step is, however, common in both reactions, namely, addition of a nucleophilic anion to an unsaturated carbon atom of the anodically generated cation radical.

Our previous studies indicate that the charge and electron density in an aromatic cation radical will be an important factor

in determining the positional reactivity in the aromatic ring.¹ Results of an MO calculation using the method of intermediate neglect of differential overlap (INDO) in the unrestricted Hartree-Fock (UHF) procedure (the INDO-UHF method) are shown in Fig. 1 for the methylanisole cation radicals. These results clearly indicate that the order of orientational preference for substitution of aromatic hydrogen of alkylanisole cation radicals may be explained in terms of the LUMO electron densities calculated for the cation radicals (*i.e.*, charge-transfer interaction) rather than net-positive-charge distributions (*i.e.*, electrostatic interaction).

The replacement of methoxy and *tert*-butyl groups during aromatic cyanation has also been observed. If the substituent already on the ring is a good cationic leaving group, *ipso*



Scheme 1

addition, the first step of *ipso* substitution by a nucleophile, can take place to a greater extent than is suggested by the LUMO electron densities.

Experimental

General.—Spectrometers and electrochemical equipment have been described previously.¹⁰

Materials.—Methanol and reagent-grade sodium cyanide were used without purification.

TBB, 4-TBA and 2-methoxy- and 4-methoxy-benzonitrile were obtained commercially. The following materials were prepared according to literature procedures: 2-TBA,¹⁶ 2,4-DTBA,¹⁷ 2,6-DTBA,¹⁸ 2,4,6-TTBA,¹⁹ 3-*tert*-butylbenzotrile **1b**⁵ and 3-*tert*-butyl-4-methoxybenzotrile **1f**.²⁰

Cyclic Voltammetry (CV).—Voltammograms were recorded for each anisole as described previously.²¹ The reference electrode was an SCE. There was no cathodic peak corresponding to reduction of an initially formed cation radical in any of the voltammograms. The E_p values are in Table 1.

Constant-current Electroreaction.—The electroreaction was carried out in a two-compartment H-type cell with a glass frit separating the compartments fitted with Pt sheet electrode (2 × 4 cm). The anolyte was made up of the organic substrate (0.02 mol), NaCN (2.0 g, 0.04 mol) and MeOH (50 cm³). The catholyte was the same medium in the absence of the substrate. The anode and cathode compartments were kept under nitrogen and the solution was stirred magnetically. The reaction was performed at 0.1 A of constant current by using a direct-current power supply at room temperature until 2.0 F mol⁻¹ of added substrate had passed through the solution.

After completion of the oxidation, the anolyte was treated with brine and extracted with diethyl ether. The extract was concentrated under reduced pressure and analysed by GLC. The columns employed for the analyses were Silicone GE SE-30 or Silicone OV-17. Each product was separated in pure form

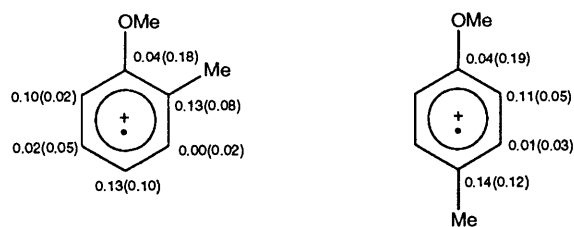


Fig. 1 LUMO electron densities and net-positive-charge densities of the cation radicals calculated by the INDO method in the unrestricted Hartree-Fock procedure. The value in parentheses represents the net-positive-charge density.

by preparative GLC. Known compounds were identified by spectral comparison with authentic samples. The structures of unknown compounds were determined by their spectroscopic characteristics and elemental analyses (Table 2). **CAUTION:** a cyanide salt in MeOH must be handled in a fume hood since it contains HCN as a result of the equilibrium between CN⁻ and the solvent MeOH.

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