tentatively suggest that the basicity enhancement of long-chain formamidines is due to this effect.

If alkyl group effects operate similarly on FDM*R and RNH_2 series, we expect a precise relationship between the gas-phase basicities of the two series. Considering the heterogeneous origin of the RNH_2 data, we observe in fact a fairly good fit (n = 14, r = 0.9751, sd = 0.70 kcal·mol^{-1}) for δGB (RNH_2) vs δGB (FDM*R), as shown on Figure 2. It is noteworthy that the cyclopropyl derivatives fit well, confirming a similar behavior in the two series. Nevertheless, the n-pentyl and n-hexyl derivatives deviate by more than one standard deviation. Further measurements are warranted before any interpretation, since the data for n-pentyl- and n-hexylamine come from a separate source (footnote h to Table II).

The directional substituent polarizability parameter σ_α was initially obtained from electrostatic polarization potentials calculated at the 3-21 G level. A simpler approach was proposed by Gasteiger and Hutchings[22] to obtain the so-called effective polarizability of substituents, α_d. They used the atomic hybrid components calculated by Miller and Savchik,[12] τ_i, weighted by a damping factor d^{n-1} which takes into account the smallest number of bonds n between the reaction site and the polarizable atom

$$\alpha_d = 4[\sum_i d^{n-1}\tau_1]^2/N \quad (6)$$

where N is the total number of electrons in the substituent. The value d = 0.75 was arrived at by investigation of several series of experimental gas-phase data. It has been shown previously that this model suffers from a deficiency for $n > 4$.[19] For example, in the sequence $(CH_2)_mCH_3$, α_d increases from m = 0 to m = 3, and then, decreases from $m > 3$ (see Table II). It has been suggested that not counting in N the electrons of atoms linked to the reaction site by more than 4 bonds may compensate for this deficiency. The modified α_d values are also given in Table II (superscript g).

In fact, we obtain a precise relationship of the form of eq 5, where α_d is substituted for σ_α: r = 0.9941, sd = 0.18 kcal·mol^{-1}, n = 8. Substituents with $n > 4$, for which α_d are anomalous, were a priori excluded. The cyclopropyl derivative was also excluded for the above mentioned reasons.

The predictive ability of the model was then tested. As expected, the calculated δGB for the cyclopropyl derivative is overestimated. The deviation from the experimental value (1.5 kcal·mol^{-1}) is to be compared with that obtained when using eq 5a (1.4 kcal·mol^{-1} for σ_α = 0.56). Substituents for which $n \leq 5$, i.e. n-butyl, cyclohexyl, and 1-adamantyl, give reasonable fit for both the original and the modified α_d values. For $n > 5$ (n-pentyl and n-hexyl) the values of Gasteiger and Hutchings are too small and cannot reasonably be used. Unfortunately, the modification of the α_d values, proposed earlier,[19] produces a too sharp increase with n, and then leads to increasingly overestimation of calculated δGBs. Further studies on rigid alkyl substituents are needed to produce a better polarizability damping model, which in turn should permit a test of the hypothesis of long chain coiling.

Conclusion

In the gas-phase FDM*R with R = alkyl are among the strongest organic bases yet known, comparable to tetramethylguanidine and 4-(dimethylamino)pyridine. Formamidines are protonated on the imino nitrogen atom. The gas-phase basicity depends linearly on the polarizability of alkyl substituents linked to the imino nitrogen. Due to the charge delocalization on the protonated amidine framework the sensitivity to this effect is reduced by a factor of about 1.7 (or 1.5) as compared to RNH_2 (or $RNMe_2$). The electron-withdrawing effect of the cyclopropyl group, as compared to the isopropyl group, on electron-rich amino and amidino systems is clearly observed. The results for n-alkyls lend support to the hypothesis of long-chain coiling.

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Anodic Oxidation of Methylbenzenes. Synthetic Routes to Certain Cyclohexa-1,4-dienes

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The anodic methoxylation of a series of methylbenzenes (mesitylene, pseudocumene, hemimellitene, pentamethylbenzene, and hexamethylbenzene) afforded chain methoxylated products as well as nuclear-addition products. For nuclear-addition products both cis/trans isomers are possible. In the cyclohexa-1,4-dienes obtained from these substrates the cis/trans ratio found is different. A probable mechanism is provided.

In the last years we have developed a series of works on anodic oxidation of alkyl aromatics[1-7] and have found that nuclear-addition products are obtained from inactivated substrates that do not stabilize the electrogenerated cation radical, showing that this type of reaction is quite general and not only observed in anthracene derivatives.[8] Some

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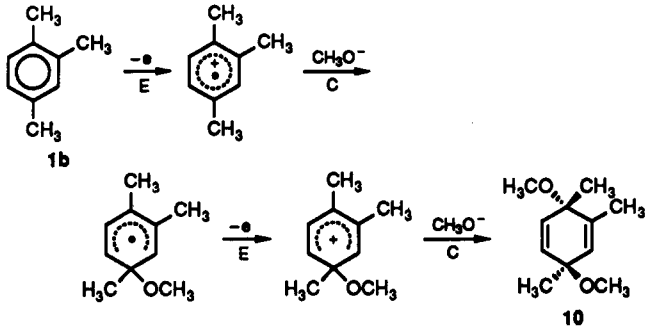
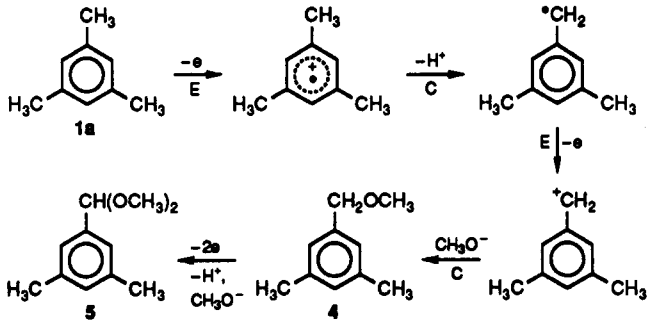
Scheme I



Scheme II



of the 1,4-diene compounds obtained can afterwards be useful in organic synthesis.[9]

Recently, in the study of pseudocumene (**1b**)[10] we have described a stereoselective 1,4-addition, that is the only case observed in the anodic methoxylation of alkylbenzenes. *trans*-Dimethoxy-1,3,6-trimethylcyclohexa-1,4-diene (**10**) was isolated as the major product, together with some side products obtained in a parallel process of side-chain substitution. Formation of product **10** was explained through a ECEC[13,14] sequence.

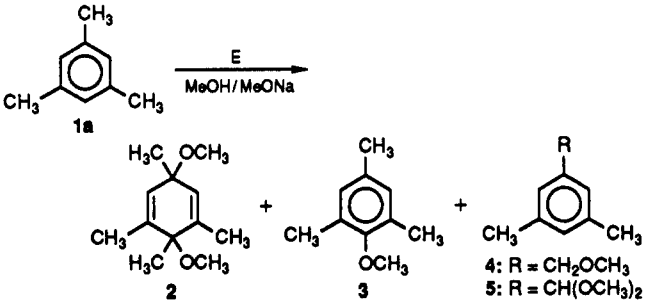
A plausible mechanism could involve adsorption if the cation formed (see Scheme I) is adsorbed with a face parallel to the anode surface via the same type of bond as in a π-donor–acceptor complex.[10] The electronegative OCH_3 group is oriented toward the positively charged electrode surface. In this way the electrode surface blocks the attack of the nucleophile and only the trans isomer is obtained.

The foregoing observations stimulated us to further explore the anodic methoxylation of a series of methylbenzenes (mesitylene, pseudocumene, hemimellitene, pentamethylbenzene, and hexamethylbenzene) under similar conditions. Although mesitylene was studied previously,[4] the different focusing of the work with 2,5-dienone compound preparation as the objective allows us to repeat its study under a different viewpoint in order to compare the mechanism reaction with those of the others methylbenzenes studied in this work, as well as to describe more reaction products.

In this paper we report the full details of a study of the stereochemistry of nuclear-addition products obtained in these anodic methoxylations and a comparison is made with the results described for pseudocumene. A probable mechanism is proposed to rationalize the results.

Results and Discussion

The anodic oxidation of mesitylene (1,3,5-trimethylbenzene) (**1a**) in methanol–sodium methoxide carried out under constant current intensity afforded a nuclear-addition product (**2**) as the major product,[4] a nuclear-substitution product (**3**),[11] and compounds **4**[12] and **5** as side-chain substitution products.



The sequence ECEC explains the formation of compounds **4** and **5** (and any side-chain methoxylated compound) as is showed in Scheme II.

The formation of **3** can be explained directly by nuclear methoxylation of mesitylene or indirectly by the same sequence previously described for pseudocumene, followed by loss of methanol from the corresponding 1,4-diene generated (unstable and not detected in the crude reaction mixture).

The nuclear trimethoxylated product **2** is formed in a second sequence ECEC with **3** as substrate. Compound **3** has the aromatic nucleus activated by the methoxy group and rapidly leads to the nuclear-trimethoxylated product **2**, through a new methoxylation process.

Compound **2** was obtained in a 55% yield. The cation radical formed in the first step of mesitylene oxidation has been found to be quite stable and has been detected by specular reflectance spectroscopy (SRS),[15] so the nucleophilic attack is favored instead of proton loss.

Acidic hydrolysis of compound **2** afforded 4-methoxy-2,4,6-trimethylcyclohexa-2,5-dienone.[4]

When the substrate was pseudocumene (1,2,4-trimethylbenzene) (**1b**), four side-chain products **6**, **7**, **8** and **9** were obtained, as well as *trans*-3,6-dimethoxy-1,3,6-trimethylcyclohexa-1,4-diene (**10**)[10] as nuclear-addition product. The ECEC sequence explains formation of these compounds. Acidic hydrolyses of compound **6** and **8** led to 2,4-dimethylbenzaldehyde and 3,4-dimethylbenzaldehyde, respectively. Orthoesters **7** and **9** afforded the corresponding methyl esters by acidic hydrolyses.

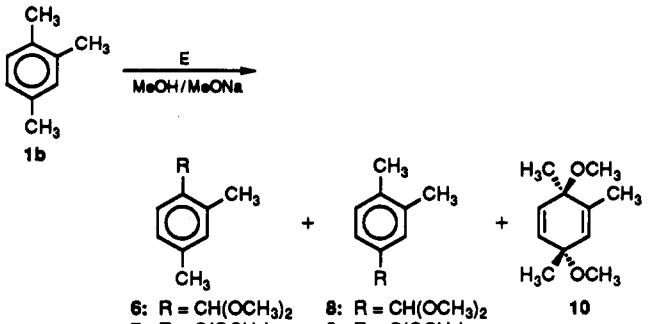


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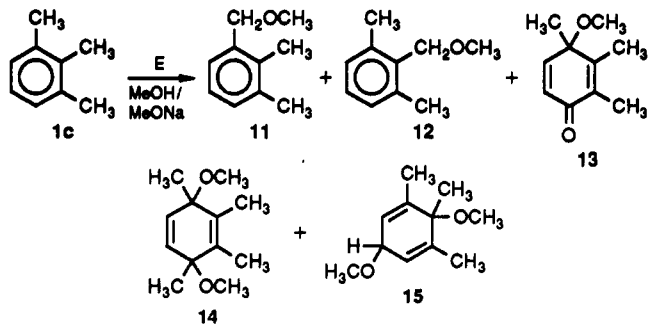
Table I

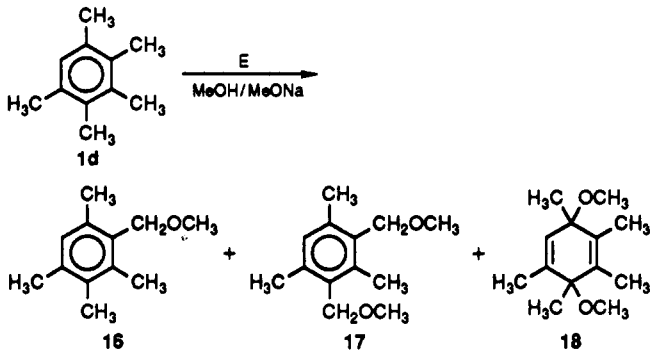
initial substrate	reaction time, min	product (yield, %)[a]
mesitylene (1a)	120	2 (55), 3 (8), 4 (2), 5 (2)
pseudocumene (1b)	180	6 (14), 7 (5), 8 (7), 9 (5), 10 (30)
hemimellitene (1c)	180	11 (11), 12 (25), 13 (8), 14 (4),[b] 15 (24)[c]
pentamethylbenzene (1d)	120	16 (44), 17 (25), 18 (21)[d]
hexamethylbenzene (1e)	120	19 (15),[c] 20 (15)[f]

[a] Deduced by GC analysis using cyclopentanone as internal standard. [b] Detected only when the temperature reaction was kept at 10–15 °C. Trans/cis ratio: 2.5/1,[c] 1.5/1,[d] 0.6/1,[e] 0.8/1.[f]

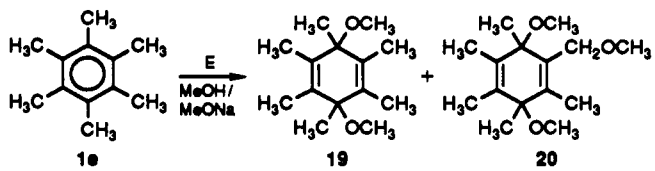
With hemimellitene (1,2,3-trimethylbenzene) (1c), the anodic oxidation led to the side-chain substitution products 11 and 12. In addition compounds 15 (trans/cis ratio = 2.5/1), 13, and 14 (detected only when the reaction temperature was kept at 10–15 °C) were obtained as nuclear-addition products. The cyclohexadienic ketal 14 is the precursor of 13 and quickly hydrolyzes even in the reaction mixture (oxidation of methanol in the anode surface liberates H^+).



The anodic methoxylation of pentamethylbenzene (1d) afforded two side-chain substitution products 16,[16] 17, and the cyclohexadiene 18. The trans/cis ratio for 18 is 1.5/1.



When the substrate was hexamethylbenzene (1e), the anodic methoxylation led to compounds 19[17] and 20 as the major products. In these compounds the cis/trans ratio obtained (Table I) shows a higher abundance of the cis isomer than the trans isomer. Polymethoxylated products were detected in the crude reaction mixture.



(16) Destina, A. N.; Mamatyuk, V. I.; Koptyug, V. A. *Zh. Org. Khim.* **1977**, *131*, 130.
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The cis and trans structures found as the reaction products above given were assigned by comparison of its ^1H NMR spectral data with those of the *trans*-3,6-dimethoxy-3,6-dimethylcyclohexa-1,4-diene unequivocally[5] identified by X-ray diffraction. These assignations were supported by the ammonia and methane chemical ionization mass spectrometry studies made with compounds 10, 15, 18, 19, and 20.[18]

Compounds 15 and 18 show a higher abundance of the trans isomer than the cis isomer. The ECEC sequence (see Scheme I) explains this ratio. The cation intermediate formed is adsorbed on the anode surface with the OMe group oriented toward the positively charged electrode surface and the formation of the trans isomer is preferred.[9]

A more recent proposal[19] involving methoxy radical attack on the cation radical generated from the substrate is the EEC_rC_p sequence (EE denotes the electrochemical steps required to form the methoxy radical and cation radical species, and C_r and C_p refers to chemical steps involving radical and polar intermediates, respectively). Formation of the intermediate cation occurs in a chemical step, and the products are formed in the bulk solution, so both cis and trans isomers could be obtained at the same rate.[5]

The sequence EEC[20] that involves a dication formed by two one-electron oxidations of the substrate and then the attack by two ^-OMe groups in a chemical step. In this case the cis isomer would be obtained as the preferred isomer.

In the formation of compounds 19 and 20 the ECEC sequence can be complemented with the participation of EEC_rC_p and EEC sequences.

Experimental Section

A generator with a maximum output of 60 V and 2 A was used. Melting points were measured on a hot-stage microscope. IR spectra are report in cm^{-1}. Nuclear magnetic resonance were recorded at 60 MHz, the chemical shifts (δ values) are given in parts per million downfield from internal tetramethylsilane (TMS, $\delta = 0$) in $CDCl_3$ solutions. Mass spectra were obtained at 70 eV (EI) and 230 eV for CI[21] (CH_4 as reagent gas). GC analysis utilized a fused silica capillary column (25 m × 0.2 nm) using nitrogen as the carrier gas (2 mL/min) and was equipped with a flame ionization detector.

Electrolysis Procedure. Electrolysis were carried out in cylindrical, water refrigerated cells without separate compartments. The temperature was controlled at 25–30 °C, and stirring was magnetic. A carbon-paste plate was used as the anode and a stainless-steel plate as the cathode. The solvent/supporting electrolyte system was prepared by adding metallic sodium (0.2 g) to dry methanol (70 mL). Reactions with the initial substrate (1 g) were carried out under constant current intensity of 1 A and an anodic density of 50 mA/cm^2, and the electron consumption was 13 F/mol (except the reactions carried out with mesitylene as substrate in which the anodic density was 63 mA/cm^2 and the electron consumption was 9 F/mol).

The electrolysis was interrupted when all starting material was consumed (followed by GC); the reaction mixture was evaporated to dryness under reduced pressure; 100 mL of a buffer solution H_3PO_4/Na_2HPO_4 (0.025 M, pH 7) was then added and the suspension was extracted with diethyl ether (3 × 30 mL). The extracts were dried (anhydrous Na_2SO_4), and the ether was evaporated at reduced pressure. Products were isolated by flash chromatography using *n*-hexane–ethyl acetate (97:3 v/v) as eluent or by chromatography on a neutral carbon–Celite column (mesitylene crude reaction) and diethyl ether as eluent.

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Acidic hydrolyses were carried out by dissolving the compounds in diethyl ether and adding to the mixture a solution of 50% hydrochloric acid. The mixture was stirred, and the organic layer was dried over anhydrous sodium sulfate and evaporated in vacuo.

The chemical structures of the acetals and orthoesters were also confirmed by comparison of the spectroscopical data of their acidic hydrolysis products with those of authentic samples.

2-Methoxymesitylene (3): ^{1}H NMR δ 2.2 (9 H, br s), 3.65 (3 H, s), 6.65 (2 H, s); MS (EI) m/e (rel intensity) 150 (M^+, 79), 135 (100), 119 (6), 107 (11), 105 (12), 91 (35), 79 (11), 77 (9).

α-Methoxymesitylene (4): ^{1}H NMR δ 2.25 (6 H, s), 3.35 (3 H, s), 4.35 (2 H, s), 7.05 (3 H, m); MS (EI) m/e (rel intensity) 150 (M^+, 93), 149 (38), 135 (100), 120 (53), 119 (99.8), 119 (41), 117 (22), 105 (59), 103 (18), 91 (62), 77 (28).

α,α-Dimethoxymesitylene (5): ^{1}H NMR δ 2.30 (6 H, s), 3.40 (6 H, s), 5.25 (1 H, s), 7.15 (3 H, m); MS (EI) m/e (rel intensity) 180 (M^+, 8), 150 (12), 149 (100), 133 (13), 119 (3), 105 (12), 91 (6), 75 (8).

1-(Dimethoxymethyl)-2,4-dimethylbenzene (6): ^{1}H NMR δ 2.25 (3 H, s), 2.3 (3 H, s), 3.3 (6 H, s), 5.35 (1 H, s), 7.1 (3 H, m): MS (EI) m/e (rel intensity) 180 (M^+, 10), 165 (1), 150 (12), 149 (100), 134 (3), 133 (14), 121 (1), 119 (3), 105 (15), 91 (6), 77 (10).

2,4-Dimethyl-1-(trimethoxymethyl)benzene (7): ^{1}H NMR δ 2.25 (3 H, s), 2.3 (3 H, s), 3.2 (9 H, s), 7.1 (3 H, m); MS (EI) m/e (rel intensity) 210 (M^+, 4), 179 (100), 148 (12), 133 (10), 105 (18), 103 (10), 91 (15), 77 (14).

4-(Dimethoxymethyl)-1,2-dimethylbenzene (8): ^{1}H NMR δ 2.25 (6 H, s), 3.3 (6 H, s), 5.35 (1 H, s); 7.05 (3 H, m); MS (EI) m/e (rel intensity) 180 (M^+, 8), 150 (13), 149 (100), 148 (4), 134 (4), 133 (16), 119 (8), 105 (18), 91 (8), 79 (9), 77 (12).

1,2-Dimethyl-4-(trimethoxymethyl)benzene (9): ^{1}H NMR δ 2.25 (6 H, s), 3.2 (9 H, s), 7.05 (3 H, m); MS (EI) m/e (rel intensity) 210 (M^+, 4), 179 (100), 148 (11), 147 (23), 105 (19), 103 (10), 91 (16), 77 (14).

2,3-Dimethyl-1-(methoxymethyl)benzene (11): ^{1}H NMR δ 2.2 (3 H, s), 2.25 (3 H, s), 3.35 (3 H, s), 4.35 (2 H, s), 7.0 (3 H, m); MS (EI) m/e (rel intensity) 150 (M^+, 10), 135 (27), 120 (6), 119 (44), 118 (100), 117 (57), 105 (26), 103 (24), 91 (69), 77 (38), 65 (20).

1,3-Dimethyl-2-(methoxymethyl)benzene (12): ^{1}H NMR δ 2.35 (6 H, s), 3.35 (3 H, s), 4.42 (2 H, s), 7.0 (3 H, m); MS (EI) m/e (rel intensity) 150 (M^+, 9), 135 (12), 120 (3), 119 (33), 118 (100), 117 (45), 103 (25), 91 (25), 77 (14).

4-Methoxy-2,3,4-trimethylcyclohexa-2,5-dienone (13): IR (film) 2940, 2840, 1670, 1640, 1100, 1050, 880, 840 cm^{-1}, ^{1}H NMR δ 1.4 (3 H, s), 1.9 (6 H, br s), 2.9 (3 H, s), 6.3 (1 H, d, J = 11 Hz), 6.3 (1 H, d, J = 11 Hz); MS (EI) m/e (rel intensity) 166 (M^+, 33), 151 (73), 138 (27), 135 (24), 123 (55), 121 (16), 108 (17), 107 (19), 106 (10), 105 (18), 95 (57), 91 (100), 77 (50), 65 (30).

3,3,6-Trimethoxy-1,2,6-trimethylcyclohexa-1,4-diene (14): MS (EI) m/e (rel intensity) 212 (M^+, 2), 197 (6), 182 (15), 181 (100), 167 (9), 166 (50), 151 (27), 150 (23), 135 (19), 123 (11), 121 (15), 105 (12), 91 (35), 79 (15).

***cis*- and *trans*-3,6-dimethoxy-1,5,6-trimethylcyclohexa-1,4-diene (15)**: IR (film) 2980, 2920, 2820, 1660, 1210, 1190, 1060 cm^{-1}; MS (EI) m/e (rel intensity) 182 (M^+, 1), 167 (35), 152 (21), 151 (100), 137 (10), 136 (51), 121 (12), 105 (21), 91 (26), 77 (17); trans isomer ^{1}H NMR δ 1.25 (3 H, s), 1.7 (6 H, s), 2.75 (3 H, s), 3.1 (3 H, s), 4.1 (1 H, m), 5.7 (2 H, m); cis isomer ^{1}H NMR δ 1.2 (3 H, s), 1.7 (6 H, s), 2.85 (3 H, s), 3.1 (3 H, s), 4.1 (1 H, m), 5.7 (2 H, m).

2-(Methoxymethyl)-1,3,4,5-tetramethylbenzene (16): IR (film) 2960, 2820, 1450, 1180, 1090, 940, 860 cm^{-1}; ^{1}H NMR δ 2.1 (3 H, s), 2.2 (3 H, s), 2.25 (3 H, s), 2.3 (3 H, s), 3.4 (3 H, s), 4.45 (2 H, s), 6.8 (1 H, m); MS (EI) m/e (rel intensity) 178 (M^+, 17), 163 (11), 146 (100), 131 (35), 117 (10), 115 (12), 91 (19).

2,4-Bis(methoxymethyl)-1,3,5-trimethylbenzene (17): IR (film) 2960, 2910, 2880, 2820, 1450, 1185, 1090, 945, 840 cm^{-1}; ^{1}H NMR δ 2.3 (6 H, s), 2.4 (3 H, s), 3.4 (6 H, s), 4.45 (4 H, s), 6.85 (1 H, s); MS (EI) m/e (rel intensity) 208 (M^+, 20), 193 (3), 177 (14), 176 (68), 163 (15), 161 (26), 147 (17), 146 (100), 145 (70), 144 (70), 133 (21), 131 (23), 130 (17), 129 (27), 128 (15), 117 (18), 115 (27), 105 (21), 91 (35).

***cis*- and *trans*-3,6-dimethoxy-1,2,3,4,6-pentamethylcyclohexa-1,4-diene (18)**: IR (film) 2980, 2820, 1640, 1090, 1050, 880, 860, 756 cm^{-1}; trans isomer ^{1}H NMR δ 1.25 (3 H, s), 1.3 (3 H, s), 1.75 (6 H, br s), 1.8 (3 H, d, J = 2 Hz), 2.8 (3 H, s), 2.85 (3 H, s), 5.5 (1 H, m); MS (EI) m/e (rel intensity) 195 (100), 180 (31), 179 (51), 165 (17), 164 (50), 149 (16), 148 (8), 147 (11), 133 (23), 115 (9), 105 (15), 91 (20), 89 (45), 77 (15); MS (CH_4-Cl, 0.5 Torr) m/e (rel intensity) 211 (M^+ + 1, 1), 209 (2), 196 (1), 195 (8), 181 (1), 180 (13), 179 (100), 177 (3), 147 (1); cis isomer ^{1}H NMR δ 1.15 (3 H, s), 1.2 (3 H, s), 1.75 (6 H, br s), 1.8 (3 H, d, J = 2 Hz), 2.9 (3 H, s), 2.95 (3 H, s), 5.5 (1 H, m); MS (EI) m/e (rel intensity) 195 (100), 180 (27), 179 (39), 165 (16), 164 (44), 149 (16), 135 (4), 133 (15), 119 (6), 115 (5), 91 (16), 89 (26); MS (CH_4-Cl, 0.5 Torr) m/e (rel intensity) 211 (M^+ + 1, 1, 209 (2), 196 (1), 195 (8), 181 (1), 179 (100), 177 (3), 165 (1), 147 (1).

***cis*- and *trans*-3,6-dimethoxy-1,2,3,4,5,6-hexamethylcyclohexa-1,4-diene (19)**: trans isomer ^{1}H NMR δ 1.25 (6 H, s), 1.70 (12 H, s), 2.75 (6 H, s); MS (EI) m/e (rel intensity) 224 (M^+, 2), 209 (29), 194 (15), 193 (48), 178 (24), 163 (14), 161 (31), 147 (15), 91 (81), 89 (100); cis isomer ^{1}H NMR δ 1.15 (6 H, s), 1.7 (12 H, s), 2.85 (6 H, s); MS (EI) m/e (rel intensity) 224 (M^+, 3), 209 (29), 194 (15), 193 (48), 178 (24), 163 (14), 161 (31), 147 (15), 91 (81), 89 (100).

***cis*- and *trans*-3,6-dimethoxy-1-(methoxymethyl)-2,3,4,5,6-pentamethylcyclohexa-1,4-diene (20)**: trans isomer ^{1}H NMR δ 1.25 (6 H, s), 1.70 (6 H, s), 1.85 (3 H, s), 2.75 (3 H, s), 2.80 (3 H, s), 3.35 (3 H, s), 3.9 (2 H, s); MS (EI) m/e (rel intensity) 254 (M^+, 1), 239 (8), 224 (2), 223 (11), 209 (5), 194 (4), 193 (23), 178 (7), 177 (39), 161 (60), 147 (12), 145 (6), 119 (10), 91 (15), 89 (100); cis isomer ^{1}H NMR δ 1.2 (6 H, s), 1.7 (6 H, s), 1.85 (3 H, s), 2.85 (3 H, s), 2.9 (3 H, s), 3.35 (3 H, s), 3.95 (2 H, s); MS (EI) m/e (rel intensity) 254 (M^+, 1), 239 (16), 223 (8), 222 (2), 210 (2), 209 (13), 194 (7), 178 (8), 177 (40), 161 (6), 147 (13), 145 (5), 119 (12), 115 (6), 105 (11), 91 (17), 89 (100).