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Cerium(IV) Ammonium Nitrate Induced Dimerization of Methoxystyrenes

Vijay Nair,[a,*] V. Sheeba,[a] Sreeletha B. Panicker,[a] Tesmol G. George,[a] Roshini Rajan,[a] Lakshmi Balagopal,[a] M. Vairamani[b] and S. Prabhakar[b]

[a]*Organic Chemistry Division, Regional Research Laboratory [CSIR], Trivandrum, 695 019, India*
[b]*Indian Institute of Chemical Technology, Hyderabad, 500 007, India*

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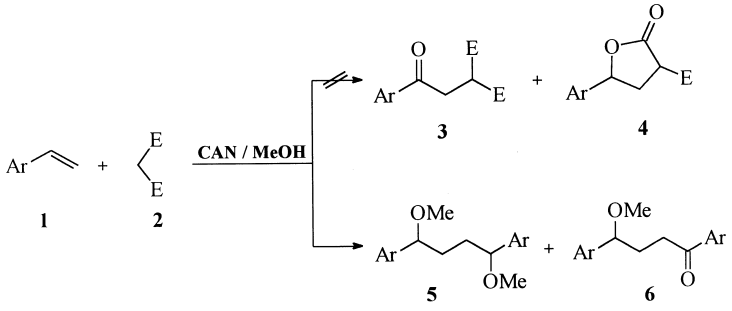
Abstract—4-Methoxystyrene **1** underwent dimerization to 1,4-diphenylbutane derivatives **5** and **6** in presence of CAN in methanol. But in ethanol the same reaction afforded a tetralone derivative along with **5** and **6**. 3,4-Dimethoxystyrene **10** underwent dimerization in presence of CAN in methanol to afford acyclic as well as cyclic products. 3,4,5-Trimethoxystyrene **12** in presence of CAN in methanol afforded only the cyclized dimers, the tetralone **21** and the tetralin derivative **22**. © 2000 Elsevier Science Ltd. All rights reserved.

Introduction

In recent years, electron transfer mediated reactions have come to the fore due to their potential to trigger transformations that are not easily accomplished by any other method.[1] Various procedures involving chemical,[2] electrochemical[3] and photochemical[4] methods can bring about electron transfer. Of the three, chemical electron transfer (CET) reactions have come to prominence only recently. The CET mediated dimerization of *N*-vinyl carbazole[5] and the recent work on carbon–carbon bond forming reactions involving cation radicals generated from alkoxy arenes[6–8] and bicyclo [2.1.0] pentanes[9] are representatives of the limited investigations in this area.

Cerium(IV) ammonium nitrate (CAN) has found extensive use in C–C bond forming reactions via radicals.[10–13] However, there is very little information available on its use in generating cation radicals.[14–16] During our investigations on CAN mediated addition of 1,3-dicarbonyl compounds to alkenes, we uncovered a novel reaction of malonate and styrene[17] resulting in a ketone and a lactone as the major products. The reaction was found to occur with various substituted styrenes. However, 4-methoxystyrene **1**, when exposed to CAN and malonate did not afford the expected products. Instead products arising from the dimerization of **1** and further transformations of the dimer were obtained. There was no evidence for the participation of malonate in this reaction (Scheme 1).

Intrigued by the ease and novelty of the process, we investigated the CAN mediated dimerization of 4-methoxystyrene



1 2 3 4 5 6

Scheme 1. Ar=4-methoxyphenyl, E=CO_2Me.

Keywords: chemical electron transfer (CET); CAN; alkoxystyrene; dimerization.
* Corresponding author. Tel.: +91-471-490406; fax: +91-471-491712; e-mail: gvn@csrrltrd.ren.nic.in

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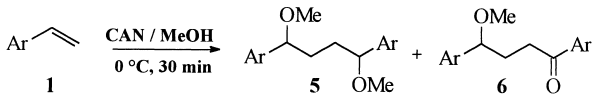


Scheme 2. Ar=4-methoxyphenyl.

Table 1.

Entry	Reaction conditions (0°C)	**5** (%)	**6** (%)
1	CAN/MeOH, air	10	53
2	CAN/MeOH, oxygen	16	62
3	CAN/MeOH, argon	60	8

and a preliminary report of our results has been published.[18] The reaction appeared interesting both from the mechanistic and synthetic standpoints. In order to assess the generality and synthetic potential of the reaction, we have carried out a systematic study involving some alkoxy styrenes and the results of our expanded investigation are presented here.

Results and Discussion

The starting point of our investigations was the reaction of 4-methoxystyrene **1** with CAN in methanol resulting in two products, **5** and **6** (Scheme 2).

Presumably **5** and **6** arise by the dimerization of the styrene via a cation radical followed by the incorporation of methanol. The keto group in **6** can be considered to arise from the oxygen in the air as evidenced from the predominance of this product when the experiment was carried out in an atmosphere of O_2. Under deoxygenated conditions **5** was found to be the predominant product (Table 1).

In ethanol, the reaction took a slightly different course leading to **7**, **8** and **9** (Scheme 3). Here too, participation of the solvent was observed though to a lesser extent (Table 2). The product **9** was characterized by the usual spectral and analytical methods. The proton bonded to the C-8 appeared as a doublet at δ 8.06 with a J value of 8.7 Hz in the proton NMR spectrum. The IR spectrum of **9** revealed the carbonyl stretching at 1667 cm^{-1} and the carbonyl carbon appeared at 196.38 in the ^{13}C NMR spectrum.

To study the generality of the reaction, the following styrenes were included in the investigation (Fig. 1).

3,4-Dimethoxystyrene **10** when treated with CAN in methanol afforded **13**, **14**, **15** and **16** (Scheme 4 and Table 3). The enhanced reactivity of the dimethoxybenzene ring predisposes it to electrophilic closure and this may account for the preferential formation of tetralone **15** and the naphthalene derivative **16**.

Table 2.

Entry	Reaction conditions (0°C)	**7** (%)	**8** (%)	**9** (%)
1	CAN/EtOH, air	48	–	26
2	CAN/EtOH, oxygen	10	13	70
3	CAN/EtOH, argon	74	–	8

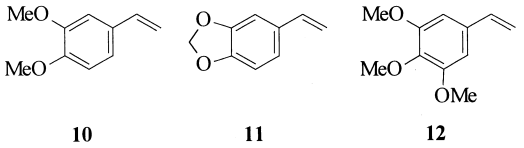
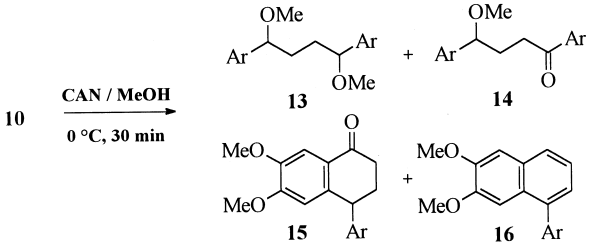


Figure 1.



Scheme 4. Ar=3,4-dimethoxyphenyl.

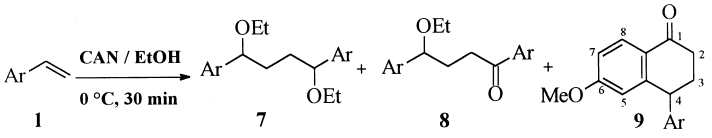
Table 3.

Entry	Reaction conditions (0°C)	**13** (%)	**14** (%)	**15** (%)	**16** (%)
1	CAN/MeOH, air	15	12	59	8
2	CAN/MeOH, oxygen	–	–	65	10
3	CAN/MeOH, argon	36	–	–	37

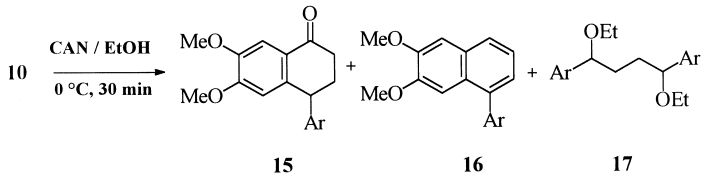
Similarly when the reaction was carried out in ethanol, **15**, **16** and **17** were obtained (Scheme 5 and Table 4). No ethoxybutanone derivative was observed in this reaction. The C-8 proton of tetralone **15** gave a characteristic signal at δ 7.59 in the ^1H NMR spectrum.

3,4-Methylenedioxystyrene **11**, when subjected to CAN in methanol at 0°C afforded a complex mixture of products. However, under deoxygenated conditions it afforded **18** in 77% yield (Scheme 6). Similarly in ethanol the diethoxybutane derivative **19** was obtained in 60% yield (Scheme 6). In oxygen saturated solvents the reaction of **11** led to a complex mixture of products.

3,4,5-Trimethoxystyrene **12**, when treated with CAN in methanol afforded **20** and **21** in 25 and 20% yields respectively. It is noteworthy that none of the products obtained are acyclic dimers. Similarly, the reaction in ethanol afforded **21** and **22** in 15 and 29% yields respectively (Scheme 7). Here **20** and **22** appear to be isomeric mixtures (according to ^{13}C NMR). These reactions were carried out



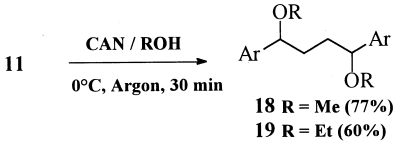
Scheme 3. Ar=4-methoxyphenyl.



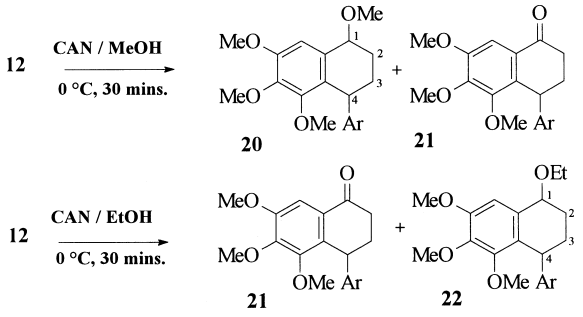
Scheme 5. Ar=3,4-dimethoxyphenyl.

Table 4.

Entry	Reaction conditions (0°C)	**15** (%)	**16** (%)	**17** (%)
1	CAN/EtOH, air	20	10	15
2	CAN/EtOH, oxygen	63	8	10
3	CAN/EtOH, argon	13	27	40



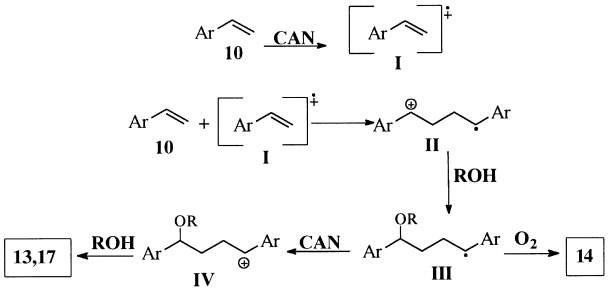
Scheme 6. Ar=3,4-methylenedioxyphenyl.



Scheme 7. Ar=3,4,5-trimethoxyphenyl.

Table 5.

Entry	Reaction conditions (0°C)	**20** (%)	**21** (%)	**22** (%)
1	CAN/MeOH, air	25	20	–
2	CAN/MeOH, oxygen	12	60	–
3	CAN/MeOH, argon	78	–	–
4	CAN/EtOH, air	–	15	29
5	CAN/EtOH, oxygen	–	55	15
6	CAN/EtOH, argon	–	–	70



Scheme 8. Ar=3,4-Dimethoxyphenyl.

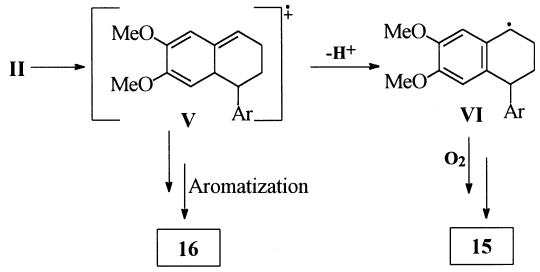
under various conditions and the results are summarized in Table 5.

Even though the mechanistic details of the reactions described herein are not known, a rationalization along the following lines may be made. The reaction of 3,4-dimethoxystyrene **10** can be taken as a representative example (Scheme 8). Styrene **10** in the presence of Ce(IV) undergoes oxidative electron transfer to afford the cation radical **I**. This in turn would add to another styrene molecule to generate a distonic radical cation **II**. Nucleophilic solvents such as methanol and ethanol can trap this cation radical **II** to generate the radical intermediate **III** This can react with oxygen from the atmosphere[21] to afford the product **14**. The radical **III** on further oxidation by Ce(IV) to a cation **IV** and subsequent trapping of the latter by solvents can afford the products **13** and **17**.

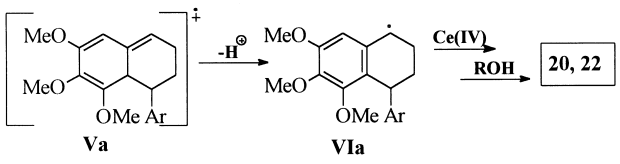
The 1,4-cation radical **II** can also undergo 1,6-cyclization to give a substituted hexatriene radical cation **V**, which on losing a proton yields the radical intermediate **VI** that can eventually transform to the tetralone **15**. The hexatriene cation radical **V** can also aromatize to afford the naphthalene derivative **16** (Scheme 9).

The tetralin derivatives **20** and **22** obtained in case of 3,4,5-trimethoxystyrene can be presumably arise from the cation radical **Va**, which is analogous to **V**. This on losing a proton generates a radical **VIa** which undergoes oxidation to a cation and the latter gets quenched by the solvent methanol or ethanol to afford the tetralin derivatives **20** and **22** respectively (Scheme 10).

It may be noted that an analogous mechanistic postulation



Scheme 9. Ar=3,4-Dimethoxyphenyl.



Scheme 10. Ar=3,4,5-Trimethoxyphenyl.

has been made for the PET mediated dimerization of 4-methoxystyrene.[19,20,22] Bauld[24] and Lewis[23] have given evidence for the formation of a long bond cyclobutane cation radical. This long bond cyclobutane cation radical can undergo a 1,3-sigmatropic shift to give the hexatriene radical cation **V**. Also Bauld et al.[24] have concluded on the basis of MNDO calculations that the cyclic dimer of the ethylene cation radical is ca. 5 kcal/mol more stable than the acyclic dimer. As shown, our results here are consistent with the mechanism proposed and proven for the PET process.

In conclusion we have uncovered a number of fascinating reactions of alkoxystyrenes initiated by the CAN mediated dimerization. These are synthetically attractive and mechanistically interesting carbon–carbon bond forming processes. The experimental simplicity and mild reaction conditions are noteworthy. It is anticipated that the processes described will find applications in organic synthesis especially in the synthesis of lignans, since most of the products reported in this paper incorporate structural frameworks present in lignans. It is noteworthy that several compounds in the lignan family are found to possess antiplatelet,[25] antiviral,[26] antitumor,[27] antidepressant[28] and insect antifeedant[29] activities.

Experimental

General

NMR spectra were recorded at 300 (^{1}H) and 75 (^{13}C) MHz. Chemical shifts are reported (δ) relative to TMS (^{1}H) and $CDCl_3$ (^{13}C) as the internal standards. Mass spectra were recorded under EI/HRMS (at 5000 resolution) using Auto Spec. M mass spectrometer. Gravity column chromatography was performed on silica gel (100–200 mesh) in hexane-ethyl acetate mixtures as the eluent. Solvents were distilled prior to use. The CAN used for the reactions was purchased from Aldrich Co. and was used without purification. The styrenes used were prepared from the corresponding aldehydes using the Wittig procedure. Commercially available ethanol and methanol were distilled prior to use.

CAN mediated oxidation of alkoxystyrenes

General procedure: A solution of CAN (1.5 mmol) in the appropriate solvent (20 mL) was added dropwise to an ice cold solution of alkoxystyrene (1 mmol) in the same solvent (20 mL). When the starting material was fully consumed (15 min), as observed by tlc, the reaction mixture was diluted with water (150 mL) and extracted with dichloromethane (3×30 mL). The combined organic extracts were pooled, washed with water, brine and dried over sodium sulfate. The solvent was removed on a rotary evaporator and the residue was subjected to column chromatography on silica gel. Elution with a mixture of ethyl acetate and petroleum ether afforded the products.

CAN mediated oxidation of alkoxystyrenes in presence of oxygen

General procedure: To an ice cooled solution of alkoxystyrene (1 mmol) in the appropriate solvent (20 mL) saturated with oxygen, an oxygenated solution of CAN (1.5 mmol) in the same solvent (20 mL) was added dropwise while the reaction mixture was continuously being purged with oxygen. The reaction mixture, on completion of the reaction, was processed as described in the general procedure given above.

CAN mediated oxidation of alkoxystyrenes in the absence of oxygen

General procedure: To an ice cooled deoxygenated (purged with argon) solution of alkoxystyrene (1 mmol) in the appropriate solvent (20 mL), a deoxygenated solution of CAN (1.5 mmol) in same solvent (20 mL) was added dropwise while the reaction mixture was continuously being purged with argon. The reaction mixture, on completion of the reaction, was processed as described in the general procedure given above.

1,4-Bis(4′-methoxyphenyl)-1,4-dimethoxybutane (5) and 1,4-bis(4-methoxyphenyl)-4-methoxybutan-1-one (6). To an ice-cooled solution of **1** (300 mg, 2.24 mmol) in methanol (20 mL), a solution of CAN (1.5 g, 2.69 mmol) in methanol (20 mL) was added dropwise. The mixture, on completion of the reaction, was processed as described in the general procedure. Column chromatography on silica gel using hexane: ethylacetate mixture as eluent afforded **5** (37 mg, 10%) and **6** (185 mg 53%).

(**5**) Colorless crystals recrystallized from hexane-dichloromethane. Mp 98–100°C; IR (KBr): 2961, 1615, 1150 cm^{-1}; ^{1}H NMR: δ 7.04 (d, J=8.6 Hz, 4H, Ar*H*), 6.74 (d, J=8.6 Hz, 4H Ar*H*), 3.87 (m, 2H C*H*OMe), 3.69 (s, 6H, ArO*Me*), 3.03 (s, 6H CHO*Me*), 1.61 (m, 4HCH_2); ^{13}C NMR: δ 159.28, 134.53, 128.12, 113.99, 83.83, 56.59, 55.47, 34.83; GC–MS (*m*/*z*) 298 (*m*/*z*) [$M^+ - HOCH_3$] (5), 266 (4), 227 (5), 166 (25), 151 (100), 135(15); Anal. Calcd for $C_{20}H_{26}O_4$: C, 72.7; H, 7.93%. Found: C, 72.64; H, 8.15%.

(**6**) Pale yellow crystals recrystallized from hexane-dichloromethane. Mp 107–108°C; IR (KBr): 2954, 1676, 1604, 1258 cm^{-1}; ^{1}H NMR: δ 7.83 (m, 2H, ArH), 7.16 (m, 2H, ArH), 4.10 (dd, J=7.7, 5.5 Hz, 1H, –C*H*OCH_3), 3.12 (s, 3H, –CHOCH_3), 3.69 (s, 6H, ArOCH_3), 2.89 (t, J=7.2 Hz, 2H, –CH_2), 2.05 (m, 2H, –CH_2); ^{13}C NMR: δ 198.83, 163.6, 159.39, 134.14, 130.52, 130.47, 128.06, 114.09, 113.89, 82.74, 56.68, 55.66, 55.49, 34.55, 32.82; Anal. Calcd for $C_{19}H_{22}O_4$: C, 72.59; H, 7.05%. Found: C, 72.38; H, 7.02%.

1,4-Bis(4′-methoxyphenyl)-1,4-diethoxybutane (7) and 4-(4′-methoxyphenyl)-6-methoxy-1-tetralone (9). To an ice-cooled solution of **1** (300 mg, 2.24 mmol) in ethanol (20 mL), a solution of CAN (1.5 g, 2.69 mmol) in ethanol (20 mL) was added dropwise. The mixture, on completion of the reaction, was processed as described in the general procedure. Column chromatography on silica gel using hexane: ethylacetate mixture as eluent afforded **7** (192 mg, 48%) and **9** (82 mg, 26%).

(**7**) Colorless oil IR: 2971, 2931, 1611, 1247 cm^{-1}; ^{1}H NMR: δ 7.16 (d, 4H, J=8.54 Hz, Ar*H*), 6.83 (d, 4H, J=8.58 Hz, Ar*H*), 4.07 (bs, 2H, C*H*OEt), 3.79 (s, 6H, ArOCH_3), 3.25 (m, 4H, OCH_2CH$_3$), 1.70 (m, 4H,

CHCH_2), 1.11 (t, 6H, J=6.98 Hz, CH_2CH_3); ^{13}C NMR: δ 159.01, 135.24, 127.79, 113.81, 81.91, 63.90, 55.23, 35.17, 15.48; HRMS Calcd for $C_{22}H_{30}O_4$: [M^+−HOEt] 312.1725. Found: [M^+−HOEt] 312.1742

(**9**) Colorless crystals recrystallized from hexane-dichloromethane. Mp 116–117°C; IR (KBr): 2953, 1667, 1596 cm^{-1}; ^{1}H NMR: δ 8.06 (d, 1H, J=8.7 Hz, Ar*H*), 7.01 (d, 2H, J=8.55 Hz, Ar*H*), 6.84 (d, 3H, J=8.66 Hz, Ar*H*), 6.41 (d, 1H, J=1.66 Hz, Ar*H*), 4.11 (dd, 1H, J=4.36, 7.44 Hz, C*H*CH_2), 3.79 (s, 3H, ArOCH_3), 3.73 (s, 3H, ArOCH_3), 2.61 (m, 2H, –COCH_2), 2.41 (m, 1H, CHCH_2), 2.29 (m, 1H, CHCH_2); ^{13}C NMR: δ 196.39, 163.58, 158.36, 148.92, 135.39, 129.56, 129.37, 126.49, 113.96, 113.49, 113.18, 55.13, 55.04, 44.82, 36.33, 31.95; HRMS Calcd for C_{18} H_{18} O_3: 282.1256. Found: 282. 1267.

1,4-Bis(4-methoxyphenyl)-4-ethoxybutan-1-one (8). The same reaction when carried out in an atmosphere of oxygen afforded **8** (83 mg, 13%) along with **7** and **9**, which were obtained in 10 and 70% yields, respectively.

(**8**) Colorless oil. IR: 2959, 1674, 1604 cm^{-1}; ^{1}H NMR: δ 7.91 (d, 2H, J=8.72 Hz, Ar*H*), 7.22 (d, 2H, J=8.5 Hz, Ar*H*), 6.90 (d, 2H, J=8.8 Hz, ArH), 6.85 (d, 2H, J=8.5 Hz, Ar*H*), 4.27 (dd, 1H, J=5.6, 7.5 Hz, C*H*OEt), 3.86 (s, 3H, ArO*Me*), 3.80 (s, 3H, ArO*Me*), 3.30 (m, 2H, –OC$H_2$$CH_3$), 2.96 (t, 2H, J=7 Hz, –C$H_2$$CH_2$–), 2.09 (m, 2H, –$CH_2CH_2$–), 1.14 (t, 3H, J=7 Hz, –OCH$_2$CH_3); ^{13}C NMR: δ 198.35, 163.21, 158.93, 134.61, 130.21, 127.57, 113.70, 113.53, 80.42, 63.817, 55.24, 55.06, 34.22, 32.81, 15.28; GC–MS (*m*/*z*) (M^+) 284 (2), 282 (20), 265 (15), 178 (10), 165 (8), 147 (10), 135 (100), 107 (8), 92 (5), 77 (10).

1,4-Bis(3′,4′-dimethoxyphenyl)-1,4-dimethoxybutane (13), 1,4-bis(3′,4′-dimethoxyphenyl)-4-methoxybutan-1-one (14), 4-(3′,4′-dimethoxyphenyl)-6,7-dimethoxy-1-tetralone (15), and 1-(3′,4′-dimethoxyphenyl)-6,7-dimethoxynaphthalene (16). To an ice-cooled solution of **10** (300 mg, 1.83 mmol) in methanol (20 mL), a solution of CAN (1.2 g, 2.19 mmol) in methanol (20 mL) was added dropwise. The reaction mixture, on completion, was processed as described in the general procedure. Column chromatography on silica gel using hexane: ethylacetate mixture as eluent afforded **13** (25 mg, 10%), **14** (185 mg, 15%), **15** (185 mg, 59%) and **16** (40 mg, 12%).

(**13**) Colorless oil. IR: 2935, 1509, 1260 cm^{-1}; ^{1}H NMR δ: 6.72 (m, 4H, Ar*H*), 6.30 (s, 2H, Ar*H*), 3.93 (m, 2H, CHO*Me*), 3.7 (s, 6H, ArO*Me*), 3.71 (s, 6H, ArO*Me*), 3.11 (s, 6H, O*Me*), 1.65 (m, 4H, CH_2); ^{13}C NMR: δ 148.55, 148.89, 146.69, 146.55, 138.78, 120.13, 111.74, 111.01, 82.45, 56.72, 55.23, 35.93; GC–MS (*m*/*z*) [M^+−2OMe] 326 (100), 295 (25), 165 (52).

(**14**) Colorless oil. IR: 1707, 1613 cm^{-1}; ^{1}H NMR: δ 7.52 (d, 1H, J=8.2 Hz, Ar*H*), 7.18 (d, 1H, J=8 Hz, Ar*H*), 6.82 (d, 1H, J=8.1 Hz, Ar*H*), 6.66 (s, 1H, Ar*H*), 6.63 (d, 1H, J=8.3 Hz, Ar*H*), 6.44 (s, 1H, Ar*H*), 4.19 (m, 1H, C*H*OCH$_3$), 3.97 (s, 3H, ArOCH_3), 3.95 (s, 3H, ArOCH_3), 3.88 (s, 3H, ArOCH_3), 3.82 (s, 3H, ArOCH_3), 3.76 (s, 3H, –OCH_3), 2.62 (m, 2H, –COCH_2–), 2.44 (m, 1H, –CHCH_2–), 2.25 (m, 1H, –CHCH_2–); ^{13}C NMR: δ 197.06, 161.62, 153.71, 153.48, 147.97, 141.20, 135.44, 133.76, 129.77, 119.87, 111.07, 56.07, 56.02, 55.96, 53.99, 44.78, 36.19, 32.44; GC–MS (*m*/*z*) (M^+) 374(26), 342(100), 343(30), 329(32), 315(65), 314(30), 283(35), 255(100), 205(32), 165(32), 115(15), 77(12), 59(15).

(**15**) Colorless oil. IR: 3002, 2942, 2847, 1681 cm^{-1}; ^{1}H NMR: δ 7.59 (s, 1H, Ar*H*), 6.82 (d, 1H, J=8.1 Hz, Ar*H*), 6.66 (s, 1H, Ar*H*), 6.63 (d, 1H, J=8.2 Hz, Ar*H*), 6.44 (s, 1H, Ar*H*), 4.19 (dd, 1H, J=4.5, 7 Hz, C*H*CH_2), 3.95 (s, 3H, ArOCH_3), 3.88 (s, 3H, ArOCH_3), 3.83 (s, 3H, ArOCH_3), 3.76 (s, 3H, ArOCH_3), 2.63 (m, 2H, COCH_3), 2.47 (m, 1H, CHCH_2), 2.24 (m, 1H, CHCH_2); ^{13}C NMR: δ 196.64, 153.61, 149.15, 148.22, 147.92, 140.99, 136.19, 126.21, 120.72, 111.55, 111.16, 110.90, 108.30, 55.90, 55.86, 55.82, 44.75, 36.08, 32.42; HRMS Calcd for $C_{20}H_{22}O_5$: 342.1467. Found: 342.1463.

(**16**) Amorphous powder. IR (KBr): 2937, 2834, 1601 cm^{-1}; ^{1}H NMR: δ 7.69 (d, 1H, J=7.98 Hz, Ar*H*), 7.35 (t, 1H, J=7.5 Hz, Ar*H*), 7.25 (m, 2H, Ar*H*), 7.15 (s, 1H, Ar*H*), 7.01 (m, 3H, Ar*H*), 4.01 (s, 3H, –OCH_3), 3.96 (s, 3H, OCH_3), 3.89 (s, 3H, OCH_3), 3.82 (s, 3H, OCH_3); ^{13}C NMR: δ 149.50, 149.37, 138.64, 133.98, 129.81, 125.84, 125.36, 123.90, 122.01, 113.24, 111.25, 106.71, 104.89, 55.98, 55.88, 55.74; HRMS Calcd for $C_{20}H_{20}O_4$: 324.1361. Found: 324. 1354.

4-(3′,4′-Dimethoxyphenyl)-6,7-dimethoxy-1-tetralone (15), 1-(3′,4′-dimethoxyphenyl)-6,7-dimethoxynaphthalene (16) and 1,4-bis(3′,4′-dimethoxyphenyl)-1,4-diethoxybutane (17). To an ice-cooled solution of **38** (300 mg, 1.83 mmol) in ethanol (20 mL), a solution of CAN (1.2 g, 2.19 mmol) in ethanol (20 mL) was added dropwise. The mixture, on completion of the reaction was processed as described in the general procedure. Column chromatography on silica gel using hexane:ethylacetate mixture as the eluent afforded **17** (60 mg, 15%) along with **15** (62 mg, 20%) and **16** (30 mg, 10%).

(**17**) Colorless oil. IR: 2943 1513, 1251, 1026 cm^{-1}; ^{1}H NMR: δ 6.69 (m, 4H, Ar*H*), 6.24 (s, 2H, Ar*H*), 4.40 (m, 1H, –C*H*OEt), 4.32 (m, 1H, C*H*OEt), 3.82 (s, 3H, ArOCH_3), 3.80 (s, 3H, ArOCH_3), 3.78 (s, 3H, ArOCH_3), 3.72 (s, 3H, ArOCH_3), 3.59 (m, 4H, OC$H_2$$CH_3$), 1.96 (m, 2H, –C$H_2$$CH_2$), 1.72 (m, 1H, –C$H_2$$CH_2$), 1.63 (m, 1H, –C$H_2$$CH_2$–), 1.22 (t, 3H, J=6.9 Hz, –OCH$_2$CH_3); ^{13}C NMR: δ 148.35, 148.65, 147.68, 147.45, 139.45, 121.02, 111.54, 111.00, 75.29, 75.16, 63.49, 55.77, 55.65, 29.68, 26.14, 15.86; GC–MS (*m*/*z*) [M^+−2OEt] 326 (100), 295 (25), 165 (52).

1,4-Bis(3′,4′-methylenedioxyphenyl)-1,4-dimethoxybutane (18). To an ice cooled deoxygenated (purged with argon) solution of **11** (300 mg, 2.03 mmol) in methanol (20 mL), a deoxygenated solution of CAN (1.33 g, 2.43 mmol) in methanol (20 mL) was added dropwise while the reaction mixture was continuously being purged with argon. The reaction mixture, on completion was processed as described in the general procedure. Column chromatography using hexane: ethylacetate mixture as the eluent afforded **18** (279 mg, 77%).

(**18**) Colorless crystals recrystallized from hexane-dichloromethane. Mp 154–156°C; IR (KBr): 2922, 1483, 1242 cm^{-1};

^{1}H NMR: δ 6.69 (m, 6H, Ar*H*), 5.94 (s, 4H, –OCH_2O–), 3.94 (brs, 2H, C*H*OMe), 3.14 (s, 6H, OCH_3), 1.68 (brs, 4H, CH_2CH_2); ^{13}C NMR: δ 147.83, 146.90, 136.19, 120.24, 107.89, 106.63, 100.90, 83.76, 83.57, 56.39, 34.58, 34.09; HRMS Calcd for $C_{20}H_{22}O_6$: 358.1416. Found: 358.1412.

1,4-Bis(3′,4′-dioxymethylenephenyl)-1,4-diethoxybutane (19). To an ice cooled deoxygenated (purged with argon) solution of **11** (300 mg, 2.03 mmol) in ethanol (20 mL), a deoxygenated solution of CAN (1.33 g, 2.43 mmol) in ethanol (20 mL) was added dropwise while the reaction mixture was continuously being purged with argon. The reaction mixture, on completion was processed as described in the general procedure. Column chromatography using hexane: ethylacetate mixture as the eluent afforded **19** (235 mg, 60%).

(**19**) Colorless oil IR: 2978, 2872, 1487, 1244 cm^{-1}; ^{1}H NMR: δ 6.69m, 6H, Ar*H*), 5.91 (s, 4H, –OCH_2O–), 4.04 (m, 1H, –C*H*OEt), 3.96 (m, 1H, –C*H*OEt), 3.66 (m, 4H, –OCH_2CH$_3$), 2.05 (m, 2H, –CH_2CH$_2$), 1.83 (m, 1H, –CH_2CH$_2$), 1.69 (m, 1H, –CH_2CH$_2$), 1.27 (m, 6H, –OCH$_2$CH_3); ^{13}C NMR: δ 148.95, 146.49, 136.28, 121.52, 107.98, 106.72, 100.77, 80.35, 63.57, 32.57, 15.93; GC–MS (*m*/*z*) [M$^+$−2OEt] 296 (2), 294 (100), 267 (15), 172 (20), 135 (50), 115 (12), 89 (8).

4-(3′,4′,5′-Trimethoxyphenyl)-5,6,7-trimethoxy-1-methoxytetralin (20) and 4-(3′,4′,5′-trimethoxyphenyl)-5,6,7-trimethoxy-1-tetralone (21). To an ice cooled solution of 12 (300 mg, 1.55 mmol) in methanol (20 mL), a solution of CAN (1.02 g, 1.85 mmol) in methanol (20 mL) was added dropwise. The reaction mixture on completion was processed as described in the general procedure. The column chromatography afforded **20** (80 mg, 25%) and *21* (62 mg, 20%).

(**20**) Colorless crystalline solid recrystallized from hexane-dichloromethane. Mp 126–127°C; IR (KBr): 2929, 1578, 1493, 1233 cm^{-1}; ^{1}H NMR: δ 6.69 (s, 1H, Ar*H*), 6.15 (s, 2H, Ar*H*), 4.24 (m, 2H, –C*H*OMe and –C*H*Ar), 3.91 (s, 3H, ArOCH_3), 3.80 (s, 3H, ArOCH_3), 3.78 (s, 3H, ArOCH_3), 3.74 (s, 3H, ArOCH_3), 3.46 (s, 3H, ArOCH_3), 3.38 (s, 3H, CHOCH_3), 1.76 (m, 4H, –CH_2CH$_2$); ^{13}C NMR: δ 152.72, 152.28, 151.46, 142.82, 142.11, 136.15, 132.31, 125.28, 107.95, 105.28, 76.27, 60.71, 60.36, 60.04, 56.42, 56.02, 55.75, 38.80, 26.45, 21.94; HRMS Calcd for $C_{23}H_{30}O_7$ 418.1991. Found: 418.2027.

(**21**) Colorless crystalline solid recrystallized from hexane-dichloromethane. Mp 114–115°C; IR (KBr): 2937, 2834, 1683, 1587, 1233 cm^{-1}; ^{1}H NMR: δ 2.2 (m, 1H, CH_2), 2.53 (m, 3H, CH_2), 3.53 (s, 3H, O*Me*), 3.75 (s, 6H, O*Me*), 3.81 (s, 3H, O*Me*), 3.92 (s, 3H, O*Me*), 3.95 (s, 3H, O*Me*), 4.57 (m, 1H, C*H*OMe), 6.23 (s, 2H, Ar*H*), 7.47 (s, 1H, Ar*H*); ^{13}C NMR: δ 197.61, 153.11, 152.76, 150.73, 147.55, 138.99, 136.60, 132.72, 128.32, 105.32, 104.88, 60.87, 60.79, 56.14, 56.04, 38.00, 33.69, 30.86; HRMS Calcd for $C_{22}H_{26}O_{7:}$ 402.1678. Found: 402.1678.

4-(3′,4′,5′-Trimethoxyphenyl)-5,6,7-trimethoxy-1-ethoxytetralin (22). To an ice cooled solution of **12** (300 mg, 1.55 mmol) in ethanol (20 mL), a solution of CAN (1.02 g, 1.85 mmol) in ethanol (20 mL) was added dropwise. The reaction mixture on completion was processed as described in the general procedure. Column chromatography afforded **21** (78 mg, 25%) and **22** (65 mg, 20%).

(**22**) Colorless oil. IR: 2942, 1596, 1507, 1235 cm^{-1}; ^{1}H NMR: δ 6.69 (s, 2H, Ar*H*), 6.16 (s, 1H, Ar*H*), 4.34 (brs, 1H, C*H*Ar), 4.25 (m, 1H, C*H*OCH$_2$CH$_3$), 3.90 (s, 3H, ArOCH_3), 3.79 (s, 3H, ArOCH_3), 3.77 (s, 3H, ArOCH_3), 3.75 (s, 3H, ArOCH_3), 3.37 (s, 3H, ArOCH_3), 2.33 (m, 1H, –CH_2CH$_2$), 1.79 (m, 3H, –CH_2CH$_2$), 1.27 (m, 3H, OCH$_2$CH_3); ^{13}C NMR: δ 14.52, 22.68, 28.11, 38.16, 54.74, 54.93, 59.13, 59.46, 62.86, 74.72, 104.08, 104.58, 106.67, 124.11, 132.56, 134.84, 142.73, 142.24, 151.04, 151.81; HRMS Calcd for $C_{24}H_{32}O_7$: 432.2148. Found: 432. 2140.

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