Carbon-Carbon Bond Cleavage of the [2.2]Paracyclophane Radical Cation Generated by Electron Transfer Oxidation with Cerium(IV) Ammonium Nitrate

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Single electron transfer (SET) oxidation of [2.2]paracyclophane (**1**) with cerium ammonium nitrate (CAN) produces the corresponding radical cation ($\mathbf{1}^{+\cdot}$), which undergoes cleavage of the carbon-carbon bond of the ethano bridge to generate the double-benzylic radical cation $\mathbf{2}^{+\cdot}$. Trapping of this intermediate by oxygen and nucleophiles gives rise to aldehydes **3**, while a second oxidation and subsequent nucleophilic trapping affords nitrates **4**. This facile cleavage of the carbon-carbon bond is explained by alignment of the latter with the π systems in the rigid structure of [2.2]paracyclophane, which enables charge delocalization across both benzene rings. When the reaction is carried out in methanol, aromatic substitution takes also place as a minor reaction pathway, which is responsible for the formation of the polyfunctionalized cyclophane **5d**.

The mode of cleavage of radical cations of 1,2-diarylethanes has been a matter of some controversy[1]. Early results obtained with cerium ammonium nitrate (CAN) oxidation of 1,2-diphenylethane pointed to the favored scission of the central carbon-carbon bond to give a benzyl radical and a benzyl cation and the products derived therefrom[2]. Photosensitized electron transfer oxidation of related systems appears to be also in agreement with an initial carbon-carbon bond cleavage[3–8]. However, more recent studies have provided support to the fact that the radical cations of 1,2-diarylethanes undergo preferential loss of a benzylic proton to give side chain-functionalized primary products[9–11]. Further oxidation of the latter in a secondary process would justify the formation of fragmentation products.

Actually, carbon-carbon bond breaking of the radical cations of 1,2-diarylethanes is enhanced in the gas phase (EI mass spectrometry), while in solution the large negative heat of solvation for the proton favors deprotonation[1]. Simple thermochemical calculations are in agreement with this rationalization[1]. Nevertheless, stereoelectronic effects must be also taken into account to explain the fragmentation mode of this type of radical cations. Thus, if for geometrical constraints the carbon-carbon instead of the carbon-hydrogen bond is aligned with the π system, fragmentation of this bond occurs despite the unfavourable thermochemistry[1].

In this context, it has been hypothesized that the radical cations of 1,2-diarylethanes have a sandwich structure, which enables charge delocalization between both benzene rings[10]. A rigid model for such sandwiched species would be the radical cation of [2.2]paracyclophane, in which alignment of the central bond of the ethano bridges with the π systems should be expected to promote carbon-carbon bond cleavage. Strain release[12,13] would substantially contribute to this process from the thermochemical point of view.

Such considerations have prompted us to investigate the Ce(IV)-induced SET oxidation of [2.2]paracyclophane in an effort to generate the double-benzylic radical cation $\mathbf{2}^{+\cdot}$ under conditions which would facilitate its trapping by oxygen and a variety of nucleophiles. Prior to our work, the oxidation of [2.2]paracyclophane has been performed by electrochemical means, but in this case products which formally arise from the double-benzylic dication $\mathbf{2}^{++}$ were mainly obtained[14]. Our present results confirm that, indeed, the radical cation $\mathbf{2}^{+\cdot}$ figures as a viable intermediate in the CAN oxidation of [2.2]paracyclophane.

Results

SET oxidation of [2.2]paracyclophane by using CAN as oxidizing reagent was conducted under a variety of experimental conditions (Table 1). The reaction was performed in chloroform, for which tetra-*n*-butylammonium hydrogen sulfate was essential as solid-liquid phase transfer catalyst, due to the scarce solubility of CAN in that solvent[15,16]. After 24 h at room temperature (entry 1) a mixture of the aldehyde **3a** and the nitrate ester **4a** was obtained (relative ratio ca. 33:67); however, at higher temperature (reflux) the only reaction product was the nitrate ester **4a** (entry 2).

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When the reaction was carried out under argon at room temperature, **4a** was again the only product (entry 3).

Table 1. Product studies of the CAN oxidation of paracyclophane (**1**)

Entry	Solvent	Conversion[a] (%)	Mass balance (%)[a,b]	Product distribution (%)[a,c] 3	4
1	$CHCl_3$	25	90	33 (**3a**)	67 (**4a**)
2	$CHCl_3$[d]	59	70	–[e]	100 (**4a**)
3	$CHCl_3$[f]	23	94	–[e]	100 (**4a**)
4	Me_2CO/H_2O (9:1)	25	92	5 (**3a**) 41 (**3b**)	54 (**4b**)
5	AcOH	57	60	12 (**3a**) 74 (**3c**)	14 (**4a**)
6	$MeOH/H_2O$ (8:2)	42	86	17 (**3d**) 45 (**3d'**)	–[g]
7	MeCN	54	68	1 (**3a**) 3 (**3b**)	2 (**4b**) 94 (**4e**)

[a] Determined by the weight of isolated products, error ca. 3% of stated value. – [b] Includes recovered **1**. – [c] Normalized to 100%. – [d] All runs at 25°C except with entry 2, which was conducted at reflux temperature. – [e] Not detected. – [f] Under argon. – [g] Not detected, but includes 38% of **5d**.

In another experiment, the oxidation of **1** was carried out in wet acetone at room temperature (entry 4), which led to a mixture of the aldehyde **3b** and the nitrate ester **4b** in almost equimolar ratio. Besides, a small amount of the aldehyde **3a** was obtained.

The next assay was performed in glacial acetic acid, also at room temperature (entry 5). Under these conditions, the aldehyde **3c** was obtained as major product, accompanied by lower amounts of the aldehyde **3a** and nitrate ester **4a**.

A further oxidation experiment was run in methanol/water (8:2). After workup in the usual way, a mixture of the aldehydes **3d** and **3d'** and the ketone **5d** was observed (entry 6). The structure of the latter polyfunctionalized product was assigned on the following basis: i) the molecular formula was $C_{19}H_{22}O_4$, as revealed by combustion analysis and exact MS measurements, ii) the ^{1}H-NMR spectrum exhibited three distinct methoxy group resonances and a characteristic AA'BB' system in the olefinic region, iii) the ^{13}C-NMR spectrum showed a peak corresponding to the carbonyl carbon and eight distinct signals in the aliphatic region and iv) the IR spectrum displayed a typical ketone absorption at 1680 cm^{-1}.

Finally, a run was made in dry acetonitrile as solvent and at room temperature. This led to the formation of the acetamide **4e** in almost quantitative yield (entry 7). Also, trace amounts of the other products (**3a, b** and **4b**) were detected.

Discussion

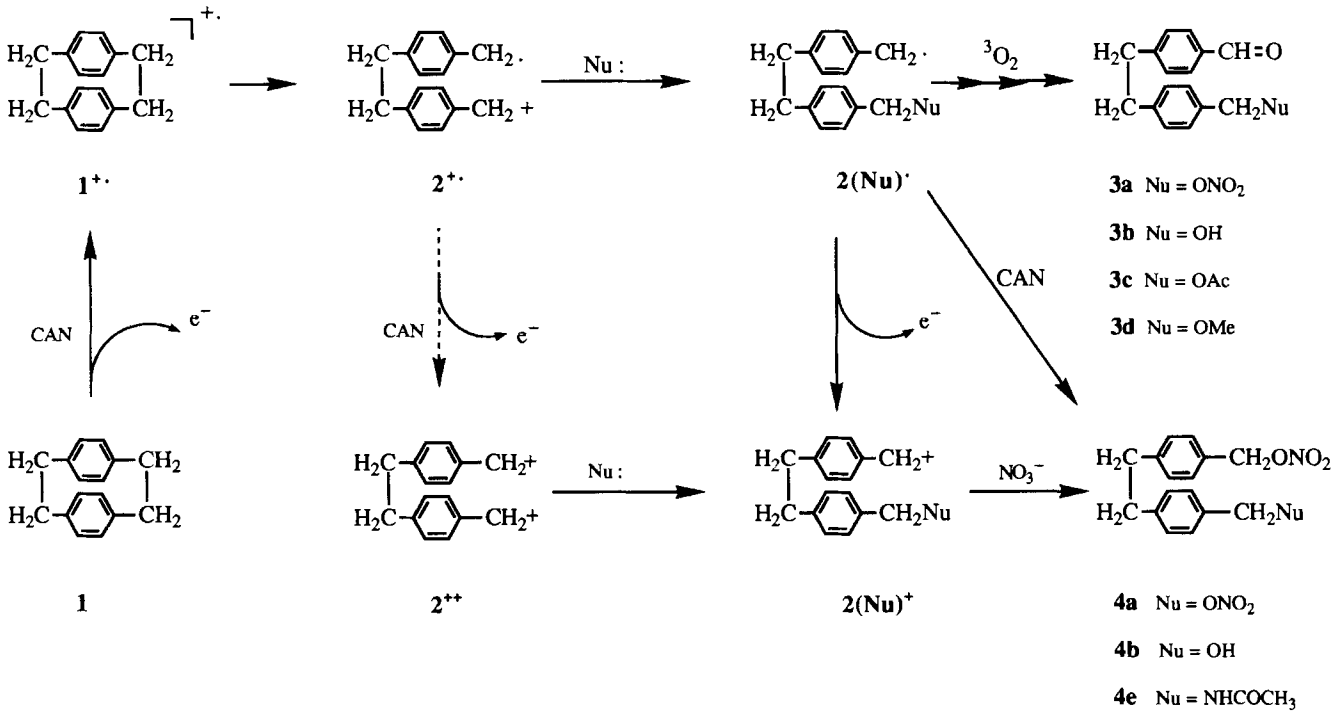
The above results are consistent with a cleavage of the radical cation of [2.2]paracyclophane ($\mathbf{1}^{+\cdot}$) to the distonic radical cation $\mathbf{2}^{+\cdot}$ as key intermediate (Scheme 1). To justify the formation of product **3a**, we propose trapping of the cationic site by the nitrate ion (the only nucleophile present in chloroform as solvent), which would lead to the benzylic nitrate ester functionality, while reaction of the radical site with molecular oxygen would generate the aldehyde moiety[17]. This pathway is reduced by heating, probably due to partial deaeration under the chloroform reflux conditions. Indeed, when the reaction is conducted under argon not even traces of **3a** are detected. To account for the dinitrate ester product **4a**, in competition with the molecular oxygen reaction of the radical **2(Nu)**$^{\cdot}$, the latter is further oxidized by CAN to the cation **2(Nu)**$^+$, which is trapped by the nitrate ion. Another possibility would be reaction of **2(Nu)**$^{\cdot}$ with CAN in an oxidative ligand transfer[18]. Control experiments showed that **3a** and **4a** were not derived from each other, since no interconversion took place when pure samples of both compounds were submitted to the same reaction conditions.

In wet acetone or acetic acid, the presence of several competing nucleophiles, i.e. the nitrate ion, water, and acetic acid, explains the role of the employed solvent. Also, acetonitrile is capable to act as a nucleophile and traps the benzylic cationic site to give the Ritter product. Again, control experiments were performed to assess the reactivity of the products under the experimental conditions. Thus, **3a**, **4a**, and **4e** were recovered unchanged after treatment with CAN in the corresponding solvents. By contrast, the alcohols **3b** and **4b** were oxidized in part to the corresponding aldehydes 1,2-bis(4-formylphenyl)ethane[19] or **3a**, respectively. The aldehyde **3c** (in acetic acid) was partially converted into an unidentified compound resulting from addition of acetic acid[20]. It is worth mentioning that the above secondary products were not detected in the reaction of **1** with CAN, with the exception of **3a**, which was obtained in very small amount (entries 4 and 7) together with its possible precursor **4b**. On the basis of these data, it can be deduced that the yields reported in Table 1 actually illustrate the primary product distribution.

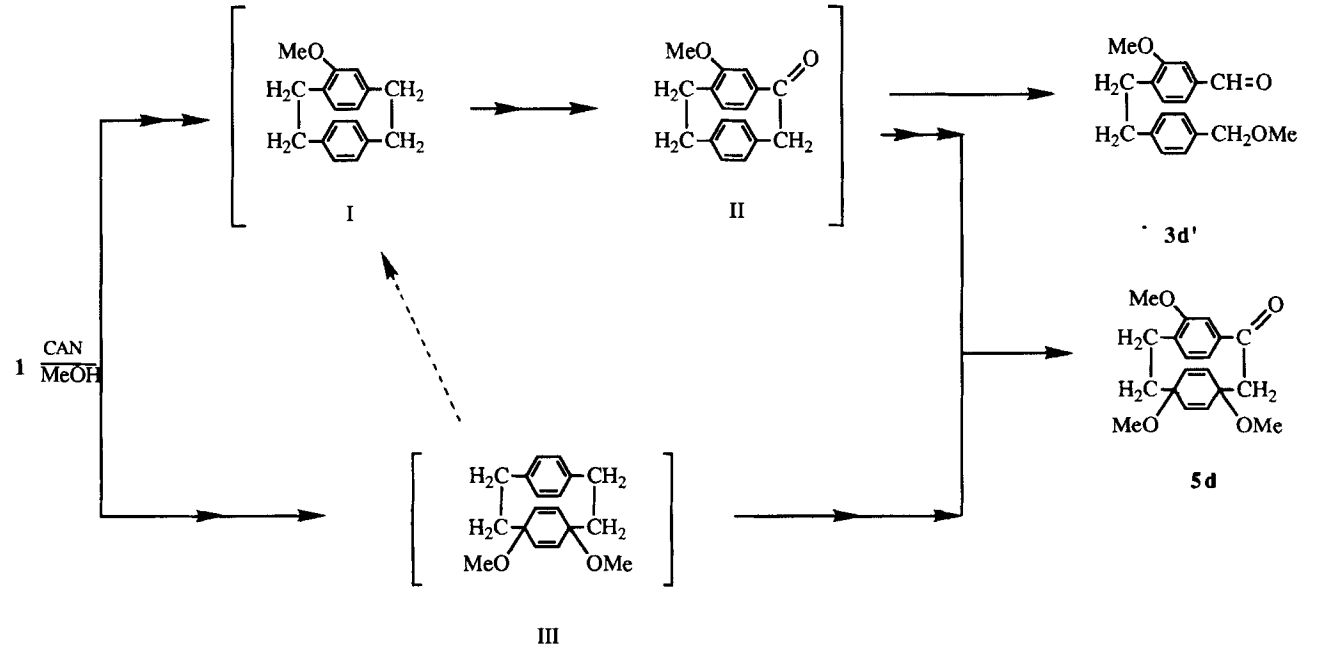
The results obtained in methanol deserve a special comment. Isolation of aldehyde **3d** is readily explained on the basis of nucleophilic trapping by methanol followed by autoxidation of **2(Nu)**$^{\cdot}$ (Scheme 1). However, aldehyde **3d'** involves aromatic substitution by methanol, which is in agreement with the reported isolation of acetoxycyclophane in the oxidation of the cyclophane **1** by lead tetraacetate[14]. This must have occurred prior to cleavage of the ethano bridge (Scheme 2), since the subsequent methoxylation of **3d** via its radical cation would be expected to occur at the electron-richer *p*-xylene-type nucleus. In fact, when **3d** was treated with CAN in methanol, no transformation occurred. The same was true for **3d'**.

Finally, for the formation of the complex product **5d** we propose the mechanism in Scheme 2, but it is difficult to ascertain the actual sequence of events; nevertheless, for all the necessary intermediary products precedents are to be found in the literature. Thus, oxidative *p*-dimethoxylation of substituted arenes is a well-established process, especially in the field of organic electrochemistry[21,22]. Furthermore, side chain oxidation of alkylarenes is also quite common,

Scheme 1



Scheme 2



and ring methoxylation under electron transfer conditions has been discussed above to justify the formation of aldehyde **3d'**. In support of the proposed mechanism in Scheme 2, it must be mentioned that GC-MS analysis of the crude reaction mixture obtained upon oxidation of cyclophane **1** in aqueous methanol allowed detection of the functionalized cyclophanes **II** and **III** in trace amounts[23]. Unfortunately, these intermediary products were formed in too small amounts to permit their isolation.

In summary, the above results show that Ce(IV) oxidation of [2.2]paracyclophane (**1**) gives rise to the corresponding radical cation $\mathbf{1}^{+\cdot}$. The most general process undergone by this species is cleavage of the carbon-carbon bond of the ethane bridge to afford the distonic radical cation $\mathbf{2}^{+\cdot}$, which is favored by alignment of this bond with the π systems of the aromatic rings.

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Experimental

Oxidation of [2.2]Paracyclophane (**1**) *with CAN in Chloroform:* To a suspension of **1** (2.00 mmol, 416 mg) and tetra-*n*-butylammonium hydrogen sulfate (0.40 mmol, 134 mg) in chloroform (50 ml) was added cerium(IV) ammonium nitrate (CAN) (4.00 mmol, 2.192 g). The mixture was stirred at room temp. for 24 h. After this time the liquid phase was decanted, and the solid residue was washed with chloroform (10 ml). The combined organic phases were washed with water (2 × 100 ml), dried ($MgSO_4$), and concentrated at reduced pressure. Column chromatography of the crude product mixture on silica gel by eluting with petroleum ether/ethyl acetate (4:1) afforded unreacted **1** (312 mg, 25% conversion), **3a** (28 mg), and **4a** (67 mg). – The reaction was repeated in refluxing chloroform for 4 h. After this time, the usual workup of the reaction mixture gave unreacted **1** (171 mg, 59% conversion) and compound **4a** (73 mg).

Oxidation of **1** *with CAN in Acetone:* A mixture of **1** (2.00 mmol, 416 mg) and CAN (8.00 mmol, 4.384 g) in 50 ml of wet acetone (water content 10%) was stirred at room temp. for 30 min. After this time the solvent was decanted and the solid washed with methanol (10 ml). Unreacted **1** (210 mg) was recovered. The combined organic extracts were poured into water (250 ml), and the precipitated white solid was collected by filtration to afford an additional 102 mg of unreacted starting material (total conversion was 25%). The filtrate was extracted with ethyl acetate (3 × 100 ml), washed with water (2 × 100 ml), dried ($MgSO_4$), and evaporated at reduced pressure. The residue was column-chromatographed as before to give **3b** (34 mg), **4b** (53 mg) and compound **3a** (5 mg) as products.

Oxidation of **1** *with CAN in Glacial Acetic Acid:* The reaction was carried out in glacial acetic acid (50 ml) and the reaction mixture worked up as above to afford unreacted **1** (180 mg, 57% conversion), **3c** (71 mg), **3a** (12 mg) and **4a** (16 mg).

Oxidation of **1** *with CAN in Acetonitrile:* The reaction was carried out in acetonitrile (50 ml). Workup as above afforded unreacted starting material (190 mg, 54% conversion), **4e** (136 mg), **3a** (1 mg), **3b** (3 mg), and **4b** (3 mg).

Oxidation of **1** *with CAN in Methanol:* A suspension of **1** (2.00 mmol, 416 mg) and CAN (8.00 mmol, 4.384 g) in a mixture of methanol (40 ml) and water (10 ml) were stirred at room temp. for 30 min. After this time the liquid phase was decanted and the remaining solid washed with methanol (10 ml) to recover 240 mg (42% conversion) of unchanged **1**. The combined liquid phases were poured into water (200 ml) and worked up as above to afford **3d** (24 mg), **3d'** (72 mg), and **5d** (67 mg).

Spectral and Analytical Data of the Oxidation Products

4-[2-(4-Formylphenyl)ethyl]benzyl Nitrate (**3a**): White crystals, m.p. 64°C (CCl_4). – IR (KBr): $\tilde{\nu}$ = 1695 cm^{-1}, 1680, 1630, 1605, 1280, 1210, 1170, 865, 855, 820, 760. – ^1H NMR (200 MHz, $CDCl_3$): δ = 9.98 (s, 1H, CHO), 7.83–7.05 (m, 8H, aromatic H), 5.40 (s, 2H, CH_2ONO_2), 2.99 (m, 4H, CH_2CH_2). – ^{13}C NMR (50 MHz, $CDCl_3$): δ = 192.0 (d), 148.5 (s), 142.5 (s), 134.5 (s), 130.0 (d), 129.4 (d), 129.2 (d), 129.0 (d), 128.8 (s), 74.7 (t), 37.8 (t), 37.0 (t). – MS (70 eV), *m/z* (%): 239 (16) [$M^+ - NO_2$], 238 (9), 223 (5), 222 (5), 210 (12), 166 (30), 165 (10), 121 (26), 120 (20), 119 (49), 91 (100), 90 (26), 89 (14), 77 (11), 65 (13). – 2,4-Dinitrophenylhydrazone: orange crystals, m.p. 182–183°C (EtOH). – $C_{22}H_{19}N_5O_7$ (465.4): calcd. C 56.77, H 4.11, N 15.04; found C 56.84, H 4.16, N 14.84.

1,2-Bis[4-(nitrooxymethyl)phenyl]ethane (**4a**): White crystals, m.p. 79°C (petroleum ether). – IR (CCl_4): $\tilde{\nu}$ = 2940 cm^{-1}, 1630, 1510, 1430, 1270, 980, 920, 850. – ^1H NMR (200 MHz, $CDCl_3$): δ = 7.28–7.14 (AA'BB', *J* = 8 Hz, 8H, aromatic H), 5.33 (s, 4H, CH_2ONO_2), 2.89 (s, 4H, CH_2CH_2). – ^{13}C NMR (50 MHz, $CDCl_3$): δ = 143.1 (s), 130.0 (s), 129.4 (d), 129.2 (d), 74.9 (t), 37.3 (t). – MS (70 eV), *m/z* (%): 270 (4) [$M^+ - ONO_2$], 240 (6), 239 (6), 210 (13), 178 (11), 166 (34), 165 (12), 149 (17), 121 (61), 120 (25), 119 (45), 118 (10), 105 (28), 104 (29), 103 (12), 95 (10), 93 (22), 92 (21), 91 (100), 90 (32), 89 (22), 81 (19), 77 (22), 69 (32), 65 (16). – $C_{16}H_{16}N_2O_6$ (332.1): calcd. C 57.82, H 4.85, N 8.42; found C 57.98, H 4.67, N 8.23.

1-(4-Formylphenyl)-2-[4-(hydroxymethyl)phenyl]ethane (**3b**): White crystals, m.p. 117–118°C (CCl_4). – IR (KBr): $\tilde{\nu}$ = 3460 cm^{-1}, 1695, 1615, 1575, 1515, 1305, 1210, 1165, 1010, 845, 820. – ^1H NMR (200 MHz, $CDCl_3$): δ = 9.97 (s, 1H, CHO), 7.83–7.11 (m, 8H, aromatic H), 4.66 (s, 2H, CH_2OH), 2.98 (m, 4H, CH_2CH_2), 1.87 (s, 1H, OH). – ^{13}C NMR (50 MHz, $CDCl_3$): δ = 192.5 (d), 148.0 (s), 140.4 (s), 138.5 (s), 134.0 (s), 129.9 (d), 129.2 (d), 128.6 (d), 127.2 (d), 65.1 (t), 38.0 (t), 37.0 (t). – MS (70 eV), *m/z* (%): 240 (2) [M^+], 179 (2), 178 (5), 149 (80), 121 (49), 119 (21), 118 (29), 103 (14), 93 (9), 91 (100), 90 (67), 89 (48), 78 (12), 77 (40), 76 (10), 69 (10), 65 (21). – $C_{16}H_{16}O_2$ (240.3): calcd. C 79.97, H 6.71; found C 79.75, H 6.51.

4-{2-[4-(Hydroxymethyl)phenyl]ethyl}benzyl Nitrate (**4b**): White needles, m.p. 94°C (CCl_4). – IR (KBr): $\tilde{\nu}$ = 3380 cm^{-1}, 1670, 1280, 1025, 1010, 865, 860, 820, 760, 680. – ^1H NMR (200 MHz, $CDCl_3$): δ = 7.34–7.12 (m, 8H, aromatic H), 5.39 (s, 2H, CH_2ONO_2), 4.65 (s, 2H, CH_2OH), 2.92 (s, 4H, CH_2CH_2), 1.78 (s, 1H, OH). – ^{13}C NMR (50 MHz, $CDCl_3$): δ = 143.4 (s), 141.0 (s), 138.6 (s), 129.8 (s), 129.4 (d), 129.1 (d), 128.8 (d), 127.3 (d), 75.0 (t), 65.3 (t), 37.7 (t), 37.4 (t). – MS (70 eV), *m/z* (%): 241 (1) [$M^+ - NO_2$], 240 (4), 225 (3), 224 (11), 163 (17), 121 (100), 120 (15), 117 (10), 105 (38), 104 (24), 103 (11), 93 (35), 91 (55). – $C_{16}H_{17}NO_4$ (287.3): calcd. C 66.89, H 5.96, N 4.87; found C 67.16, H 5.72, N 4.55.

2-[4-(Acetoxymethyl)phenyl]-1-(4-formylphenyl)ethane (**3c**): White plates, m.p. 58–60°C (heptane). – IR (KBr): $\tilde{\nu}$ = 1740 cm^{-1}, 1695, 1605, 1380, 1260, 1230, 1210, 1170, 1030, 1015. – ^1H NMR (200 MHz, $CDCl_3$): δ = 9.97 (s, 1H, CHO), 7.83–7.11 (m, 8H, aromatic H), 5.08 (s, 2H, CH_2OCOCH_3), 2.98 (m, 4H, CH_2CH_2), 2.10 (s, 3H, $COCH_3$). – ^{13}C NMR (50 MHz, $CDCl_3$): δ = 192.0 (d), 171.5 (s), 148.9 (s), 141.0 (s), 134.6 (s), 133.8 (s), 129.9 (d), 129.2 (d), 128.6 (d), 128.5 (d), 66.1 (t), 37.9 (t), 37.0 (t), 21.0 (q). – MS (70 eV), *m/z* (%): 282 (2) [M^+], 240 (20), 239 (60), 222 (10), 178 (10), 163 (82), 135 (16), 121 (100), 120 (32), 119 (21), 118 (16), 117 (28), 105 (18), 104 (33), 103 (18), 93 (19), 91 (90), 89 (20), 77 (43), 65 (19), 63 (10), 57 (13), 43 (88). – $C_{18}H_{18}O_3$ (282.3): calcd C 76.57, H 6.42; found C 76.29, H 6.30.

1-(4-Formylphenyl)-2-[4-(methoxymethyl)phenyl]ethane (**3d**): White plates, m.p. 60–61°C ($CHCl_3$). – IR (KBr): $\tilde{\nu}$ = 1695 cm^{-1}, 1630, 1605, 1575, 1450, 1380, 1305, 1280, 1210, 1200, 1165, 1100, 845, 820. – ^1H NMR (200 MHz, $CDCl_3$): δ = 9.98 (s, 1H, CHO), 7.93–7.02 (m, 8H, aromatic H), 4.43 (s, 2H, CH_2OCH_3), 3.39 (s, 3H, OCH_3), 2.98 (m, 4H, CH_2CH_2). – ^{13}C NMR (50 MHz, $CDCl_3$): δ = 192.2 (d), 149.2 (s), 140.6 (s), 136.3 (s), 134.8 (s), 130.1 (d), 129.4 (d), 128.7 (d), 128.1 (d), 74.7 (t), 58.2 (q), 38.1 (t), 37.2 (t). – MS (70 eV), *m/z* (%): 254 (5) [M^+], 223 (1), 178 (2), 135 (100), 134 (11), 105 (25), 104 (8), 103 (12), 91 (32), 77 (7), 65 (6). – 2,4-Dinitrophenylhydrazone: orange crystals, m.p. 189–191°C

(EtOH). – $C_{23}H_{22}N_4O_5$ (434.4): calcd. C 63.58, H 5.09, N 12.89; found C 63.47, H 5.05, N 12.89.

1-(4-Formyl-2-methoxyphenyl)-2-[4-(methoxymethyl)phenyl]-ethane (**3d'**): Colorless, viscous oil. – IR (KBr): $\tilde{\nu}$ = 1685 cm^{-1}, 1600, 1580, 1500, 1260, 1110, 1025, 815, 620. – ^1H NMR (200 MHz, $CDCl_3$): δ = 9.84 (s, 1H, CHO), 7.73 (dd, $J_{3,5}$ = 2, $J_{5,6}$ = 8 Hz, 1H, aromatic 5-H), 7.64 (d, $J_{3,5}$ = 2 Hz, 1H, aromatic 3-H), 7.25 and 7.17 (AA'BB', J = 8 Hz, 4H, aromatic H), 6.95 (d, $J_{5,6}$ = 8 Hz, 1H, aromatic 6-H), 4.43 (s, 2H, CH_2OCH_3), 3.90 (s, 3H, Ar-OCH_3), 3.37 (s, 3H, CH_2OCH_3), 2.91 (m, 4H, CH_2CH_2). – ^{13}C NMR (50 MHz, $CDCl_3$): δ = 191.1 (d), 163.0 (s), 141.3 (s), 135.7 (s), 131.2 (s), 130.9 (d), 129.6 (s), 128.5 (d), 127.9 (d), 110.1 (d), 74.6 (t), 58.0 (q), 55.7 (q), 35.5 (t), 32.2 (t). – MS (70 eV), *m/z* (%): 284 (12) [M^+], 267 (6), 253 (6), 252 (18), 178 (4), 165 (4), 149 (59), 135 (59), 121 (28), 120 (10), 119 (33), 105 (27), 104 (36), 103 (21), 91 (100), 89 (13), 78 (25), 77 (28), 65 (28). – 2,4-Dinitrophenylhydrazone: orange crystals, m.p. 167–168°C (EtOH). – $C_{24}H_{24}N_4O_6$ (464.4): calcd. C 62.06, H 5.20, N 12.06; found C 62.25, H 5.14, N 12.17.

4-(2-{4-[(Acetylamino)methyl]phenyl}ethyl)benzyl Nitrate (**4c**): White crystals, m.p. 125–127°C (CCl_4). – IR (CCl_4): $\tilde{\nu}$ = 2940 cm^{-1}, 2890, 1630, 1510, 1430, 1415, 1270, 975, 920, 845. – ^1H NMR (200 MHz, $CDCl_3$): δ = 7.34–7.15 (m, 8H, aromatic H), 5.75 (s, 1H, NH), 5.40 (s, 2H, CH_2ONO_2), 4.40 (s, 2H, CH_2NH), 2.93 (s, 4H, CH_2CH_2), 2.04 (s, 3H, $COCH_3$). – ^{13}C NMR (50 MHz, $CDCl_3$): δ = 170.0 (s), 143.3 (s), 140.9 (s), 136.1 (s), 129.9 (s), 129.5 (d), 129.1 (d), 128.9 (d), 128.1 (d), 74.9 (t), 43.5 (t), 37.7 (t), 37.4 (t), 23.3 (q). – MS (70 eV), *m/z* (%): 266 (16) [M^+ – ONO_2], 265 (18), 238 (44), 163 (14), 162 (97), 161 (88), 121 (25), 120 (100), 119 (76), 103 (12), 93 (30), 91 (61), 90 (17). – $C_{18}H_{20}N_2O_4$ (328.3): calcd. C 65.84, H 6.13, N 8.53; found C 65.57, H 5.86, N 8.53.

3,4,7-Trimethoxy-2-oxotricyclo[8.2.2.2^{4,7}]hexadeca-5,10,12,13,15-pentaene (**5d**): Colorless, viscous oil. – IR (KBr): $\tilde{\nu}$ = 2930 cm^{-1}, 1680, 1620, 1580, 1505, 1460, 1445, 1330, 1260, 1080. – ^1H NMR (200 MHz, $CDCl_3$): δ = 7.77 (d, $J_{3,5}$ = 2 Hz, 1H, aromatic 3-H), 7.62 (dd, $J_{3,5}$ = 2, $J_{5,6}$ = 8 Hz, 1H, aromatic 5-H), 6.83 (d, $J_{5,6}$ = 8 Hz, 1H, aromatic 6-H), 5.69 and 5.48 (AA'BB', J = 11 Hz, 4H, CH=CH), 3.85 (s, 3H, Ar-OCH_3), 3.35 (s, 2H, CH_2CO), 3.18 (s, 3H, OCH_3), 3.01 (s, 3H, OCH_3), 2.85 (m, 2H, $ArCH_2CH_2$), 2.05 (m, 2H, $ArCH_2CH_2$). – ^{13}C NMR (50 MHz, $CDCl_3$): δ = 197.5 (s), 160.8 (s), 137.8 (d), 134.3 (d), 133.7 (d), 129.4 (s), 128.3 (s), 127.1 (d), 110.4 (d), 72.9 (s), 72.7 (s), 55.8 (t), 55.5 (q), 51.9 (q), 50.8 (q), 40.8 (t), 25.9 (t). – MS (70 eV), *m/z* (%): 314 (45) [M^+], 285 (1), 284 (5), 269 (4), 241 (2), 223 (2), 178 (2), 176 (7), 165 (7), 163 (27), 161 (15), 152 (15), 151 (88), 149 (4), 148 (6), 147 (6), 139 (5), 138 (11), 134 (17), 133 (28), 123 (19), 122 (8), 121 (100), 120 (17), 119 (15), 118 (10), 117 (11), 115 (10), 108 (5), 106 (6), 105 (25), 104 (21), 103 (20), 92 (9), 91 (59), 90 (18), 89 (26), 78 (50), 77 (58), 67 (3), 65 (31). – $C_{19}H_{22}O_4$ (314.2): calcd. C 72.59, H 7.05; found C 71.80, H 7.13. Exact mass analysis: calcd. 314.1518; found 314.1526 (MS).

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[23] **II**: MS, *m/z* (%): 252 (78), 148 (42), 120 (70), 105 (39), 104 (65), 103 (55), 90 (54), 89 (53), 78 (78), 77 (100). – **III**: MS, *m/z* (%): 270 (11), 134 (10), 121 (100), 91 (24), 78 (15), 77 (11).

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