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Synthesis and reactions of nitro derivatives of hydrogenated cardanol

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Abstract—3-*n*-Pentadecylphenol (hydrogenated cardanol) and its derivative 5-*n*-pentadecyl-2-*tert*-butylphenol can be nitrated using nitric acid in acetonitrile or methanol to give mono, di or trinitro products. 5-*n*-Pentadecyl-2-nitrophenol undergoes reductive carbonylation to give a benzoxazole-2-one derivative. An efficient catalytic oxidation reaction in the presence of $MeReO_3$ has also been studied.

1. Introduction

In recent years an increasing amount of work on cashew nut shell liquid derivatives has appeared in the literature. Cashew nut shell liquid (CNSL) is obtained as a by-product from mechanical processing for edible use of cashew kernel (*Anacardium occidentale* L.) and is a mixture of anacardic acid **1**, cardanol **2** and smaller amounts of cardol **3** and 2-methylcardol **4**.[1] Due to the easy thermal decarboxylation of anacardic acid **1**, the main component of distilled CNSL is cardanol **2** (yield up to 70–80% and purity up to 90%) as a mixture of saturated (3-*n*-pentadecylphenol), monoolefinic [3-(*n*-pentadeca-8-enyl)phenol], diolefinic [3-(*n*-pentadeca-8,11-dienyl)phenol], and triolefinic [3-(*n*-pentadeca-8,11,14-trienyl)phenol] long-chain phenols, with an average value of two double bonds per molecule. Cardol **3** and methylcardol **4** are present in smaller percentages (Fig. 1).[2]

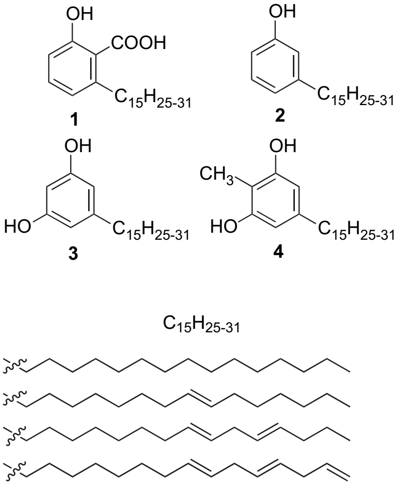

Figure 1. Components of CNSL.

World-wide cashew nut production is presently estimated to be 1,200,000 tons per annum and the availability of CNSL is 300,000–360,000 tons per annum. As the production of cashew nuts is rising every year the availability of up to 600,000 tons per annum of CNSL should be reached in the near future. Cardanol, upon catalytic hydrogenation, yields 3-*n*-pentadecylphenol (hydrogenated cardanol) and this unique alkyl phenol derivative is produced commercially in high purity.[3] Owing to the difficulty of synthesizing long-chain alkyl phenols with an aliphatic chain in the *meta* position, hydrogenated cardanol represents a simple and easily available entry to various derivatives useful for different purposes (e.g., antioxidants, flame-retardants, waterproofing agents, gum inhibitors for gasoline). Recently we have reported allylation and regioselective cyclocarbonylation[4] reactions on hydrogenated cardanol and the preparation of phthalocyanines,[5] porphyrins[6] and fullerene[7] derivatives of cardanol that possess lower melting points and higher solubility than similar products lacking long alkyl side-chains. Even azocrown ethers have been prepared from cardanol derivatives.[8] So these derivatives are an attractive

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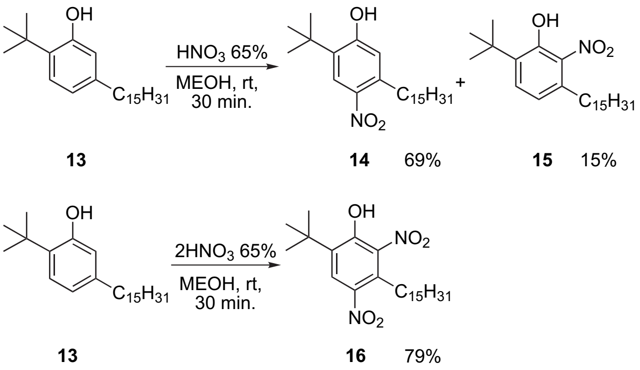
renewable bio-source to develop new eco-friendly functional materials.

2. Results and discussion

2.1. Nitration of cardanol derivatives

In this paper we describe a mild and efficient protocol for the nitration of 3-*n*-pentadecylphenol **5** and its derivative 5-*n*-pentadecyl-2-*tert*-butylphenol **13**.[2] Nitration of cardanol derivatives has been carried out some time ago but only a few products[9] have been reported and a complete study of this interesting reaction has not been conducted until now. Nitro derivatives are useful materials and are very important intermediates in organic synthesis, especially in the preparation of amino derivatives. Some patents are related to preparation of 5-*n*-pentadecyl-2-nitrophenol **6** and 3-*n*-pentadecyl-4-nitrophenol **7** but the synthetic utility of other products from the nitration process has not been described.[10] Therefore, we undertook the study of reactions between hydrogenated cardanol and nitric acid.

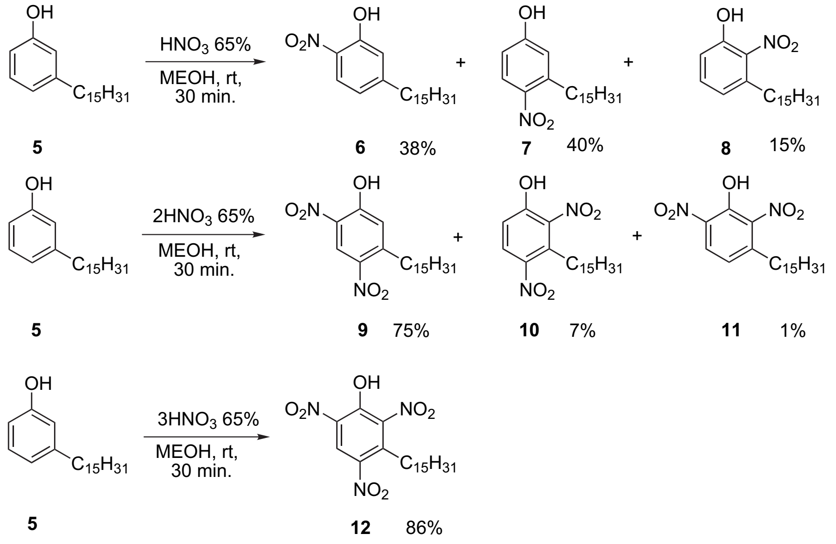
The reactions proceeded smoothly at room temperature, under mild conditions, with a stoichiometric amount of nitric acid with easy work-up procedures. 3-*n*-Pentadecylphenol **5** reacted in 30 min at room temperature in acetonitrile or methanol with an equimolar amount of nitric acid (65%). After work-up procedures and chromatographic separations of the reaction mixture, 5-*n*-pentadecyl-2-nitrophenol **6** (38%), 3-*n*-pentadecyl-4-nitrophenol **7** (40%) and 3-*n*-pentadecyl-2-nitrophenol **8** (15%) were obtained. Under the same experimental conditions, 3-*n*-pentadecylphenol **5** reacted with nitric acid (65%) in a molar ratio 1:2 and 5-*n*-pentadecyl-2,4-dinitrophenol **9** was isolated in high yields (75%) along with small quantities of two other isomers 3-*n*-pentadecyl-2,4-dinitrophenol **10** (7%) and 3-*n*-pentadecyl-2,6-dinitrophenol **11** (1%) (GC–MS), due to steric hindrance of position 2 of 3-*n*-pentadecylphenol. When the ratio 3-*n*-pentadecylphenol/nitric acid (65%) was increased to 1:3 the only recovered reaction product was 3-*n*-pentadecyl-2,4,6-trinitrophenol **12** in high yields (86%) (Scheme 1). TGA/DSC on 3-*n*-pentadecyl-2,4,6-trinitrophenol **12** were carried out (see Section 4). 5-*n*-Pentadecyl-2-*tert*-butylphenol **13** reacted in 30 min at room temperature in acetonitrile or methanol with an equimolar amount of nitric acid (65%) affording a reaction mixture that after work-up procedures and chromatographic separations furnished 2-*tert*-butyl-5-*n*-pentadecyl-4-nitrophenol **14** (69%) and 3-*n*-pentadecyl-6-*tert*-butyl-2-nitrophenol **15** (15%). 5-*n*-Pentadecyl-2-*tert*-butylphenol **13** reacted with nitric acid (65%) in a molar ratio 1:2 affording 3-*n*-pentadecyl-6-*tert*-butyl-2,4-dinitrophenol **16** (79%) (Scheme 2).



Scheme 2.

2.2. $MeReO_3$ oxidation of cardanol derivatives

In spite of the high number of synthetic transformations reported for cardanol derivatives,[11] to the best of our knowledge there are few catalytic oxidative procedures. In this context, we described a convenient and efficient application of the catalytic system $MeReO_3/H_2O_2$ for the preparation of *ortho*- and *para*-benzoquinones from cardanol derivatives.[12] The regioselectivity of these oxidations was found to be dependent on the nature and position of substituents on the aromatic ring, *ortho*-benzoquinones being obtained only in the absence of an alkyl substituent on the C-2 position of the aromatic ring.



Scheme 1.

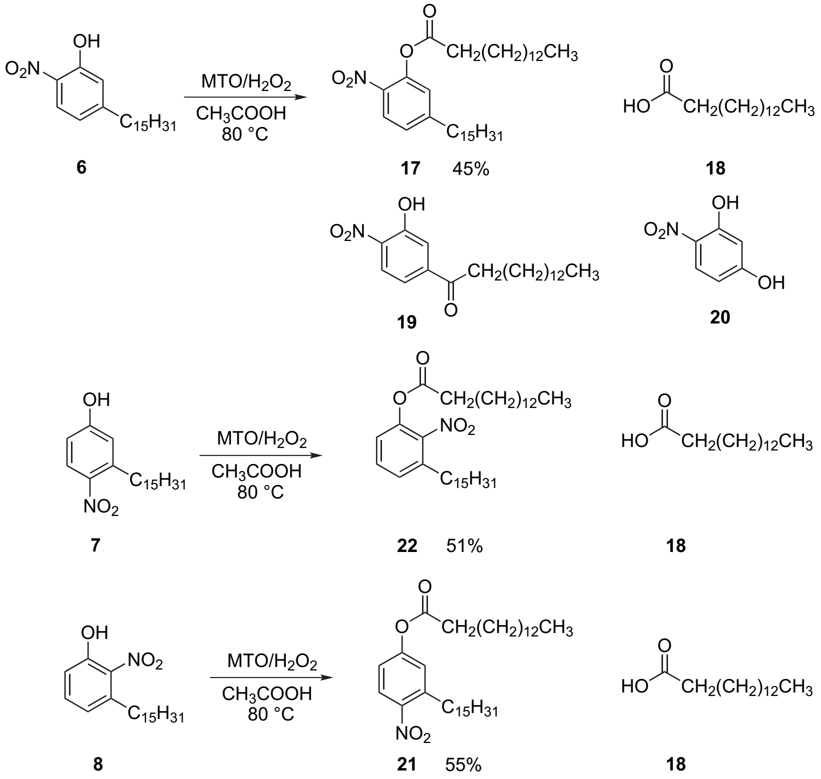
In the past few years methylrhenium trioxide ($MeReO_3$, MTO)[13] has been shown to possess interesting catalytic properties in oxidation reactions with environmental friendly hydrogen peroxide (H_2O_2) as an oxygen atom donor.[14] Methoxy-substituted benzenes are oxidized with the $MeReO_3/H_2O_2$ system in acetic acid to yield the corresponding alkoxy-substituted *para*-benzoquinones,[15] some of which show important biological activities.[16] Cardanol derivatives bearing bromine atoms as electron-withdrawing substituents were also found to be reactive substrates under these experimental conditions to give *para*-benzoquinone or catechol derivatives. A similar behaviour was observed with polymer supported rhenium catalysts based on the heterogenation of $MeReO_3$ on poly(4-vinylpyridine) 2% and 25% (PVP-2, PVP-25) cross-linked with divinylbenzene.[17] Higher conversions and yields of benzoquinones were obtained with PVP heterogeneous catalysts than with $MeReO_3$ in homogeneous phase, probably because of a support-mediated molecular recognition process based on hydrogen-bonding interactions between the pyridinyl moiety and the phenolic group of cardanol.[18]

Moreover, during the oxidation of cardanol derivatives with novel microencapsulated $MeReO_3$ systems, an unprecedented oxidative degradation of the aromatic moiety to biologically active γ-lactone derivatives was observed in the absence of C-2 substituents.[17]

We report here that $MeReO_3$ is an efficient and selective catalyst for the activation of H_2O_2 in the oxidation of relatively unreactive nitrocardanol derivatives. Because of the high value of the redox-potential of the aromatic moiety of these compounds, the oxidation proceeded mainly in the alkyl side-chain to give unexpected *O*-pentadeca-acyl cardanol derivatives probably by a side-chain intermolecular transfer process between two molecules of substrate.

Oxidations were performed by treating the appropriate substrate with an excess of H_2O_2 (8.0 equiv 35% aqueous solution) in acetic acid (1.0 mL) at 80 °C in the presence of catalytic amount of $MeReO_3$ (2% in weight of catalyst). Results of oxidations are reported in Scheme 3 and Table 1. The oxidation of 5-*n*-pentadecyl-2-nitrophenol **6** gives *O*-pentadecanoyl-5-*n*-pentadecyl-2-nitrophenol **17**, as the main reaction product, besides a low amount of pentadecanoic acid **18** as side-product (Table 1, entry 1).

Traces of aromatic ketone derivative **19** and 1,3-dihydroxy-6-nitrobenzene **20** were also detected in the reaction mixture by GC–MS analysis (see Scheme 3 for structures of compounds **19** and **20**) after derivatization with *N*,*O*-bis-trimethylsilyltrifluoroacetamide (BSTFA). It is reasonable to suggest that compound **17** can be formed by an intermolecular acyl transfer process from a first formed side-chain oxidized product. In particular, the reaction initially may proceed through oxidation of the reactive benzylic position to give **19**. The catalytic efficacy of $MeReO_3$ to afford a Bayer–Villinger rearrangement is known from the literature. In accordance with these data, ketone **19** can be further oxidized to corresponding aryl ester derivative (not shown), which can act as an electrophilic species transferring the acyl side-chain to a second molecule of substrate to give compounds **17** and **20**. In accordance with this hypothesis, treatment of a small amount of isolated ketone **19** with MTO under similar conditions afforded compounds **17** and **20** in detectable amounts. The hypothesized reaction



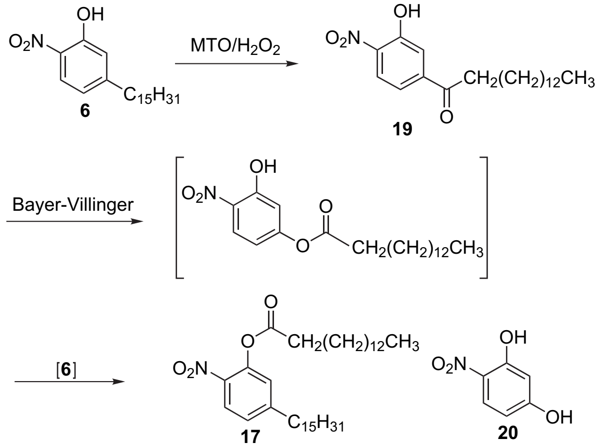
Scheme 3.

Table 1. Oxidation of nitrocardanol derivatives **6–8**, **15** with $MeReO_3$ and H_2O_2[a]

Entry	Substrate	H_2O_2 (equiv)	Conversion (%)	Product(s)	Yield(s)
1	**6**	6.0	75	**17**(**18**)	45(8)
2	**7**	6.0	55	**22**(**18**)	51(6)
3	**8**	6.0	65	**21**(**18**)	55(6)
4	**15**	6.0	70	**23**(**24**)	25(26)

[a] Reactions were performed with an excess of H_2O_2 (8.0 equiv) in CH_3COOH (1 mL) in the presence of 2% in weight of $MeReO_3$. Yields are calculated on converted substrate. The low mass-balance observed in some cases, is probably due to the formation of over-oxidation products not recovered under our experimental conditions.

pathway for the oxidation of **6** is schematically reported in Scheme 4.

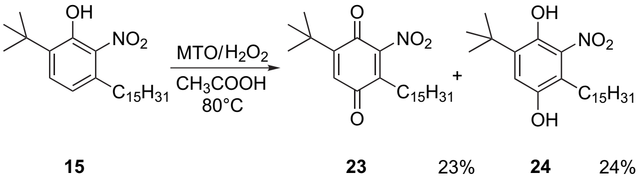


Scheme 4.

The low mass-balance observed for compound **20** is probably due to formation of high-polarity over-oxidation products not detectable under our experimental conditions. To the best of our knowledge this is one of the few examples of a multifunctional catalytic behaviour showed by $MeReO_3$ during the oxidation of natural substances with H_2O_2 as primary oxidant. To evaluate the generality of this transformation isomeric nitrocardanol derivatives 3-*n*-pentadecyl-4-nitrophenol **7** and 3-*n*-pentadecyl-2-nitrophenol **8** were oxidized under similar experimental conditions. Irrespective of the position of the nitro substituent on the aromatic ring, the corresponding *O*-acyl derivatives, *O*-pentadecanoyl-3-*n*-pentadecyl-4-nitrophenol **21** and *O*-pentadecanoyl-3-*n*-pentadecyl-2-nitrophenol **22**, were recovered as the main reaction products in acceptable yields (Table 1, entries 2 and 3).

In accordance with data previously obtained on the oxidation of cardanol derivatives with $MeReO_3$,[12] the presence of an alkyl substituent on the C-2 position of the aromatic ring modified the selectivity of the reaction.

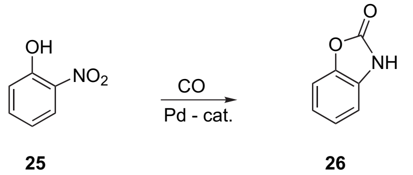
Thus, the oxidation of 3-*n*-pentadecyl-6-*tert*-butyl-2-nitrophenol **15**, performed under similar experimental conditions, gave the *para*-benzoquinone **23** and *para*-hydroquinone **24** as main products. (Scheme 5, Table 1, entry 4). In this case O-acylated products were not observed in the reaction mixture suggesting that the presence of the electron-donating alkyl substituent enhances the redox-potential of the aromatic ring, as would be expected.



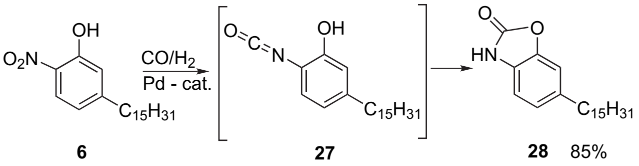
Scheme 5.

2.3. Reductive carbonylation of 5-*n*-pentadecyl-2-nitrophenol

Benzoxazolinones are a known class of commercially available compounds that are widely used in agriculture and industry. Traditionally, these compounds are produced by the intramolecular cyclization of phenyl *N*-(2-hydroxyphenyl) carbamate, which is produced by the reaction of *ortho*-aminophenol with phenyl chloroformate.[19] This route needs a large number of steps from commercially available starting materials. Various catalytic systems have been found for the preparation of benzoxazolinone in one step from readily available starting materials. For example, Fe/Pd as well as $Na_2[Fe(CO)_4]$ were used as catalysts for the reductive cyclocarbonylation of *ortho*-nitrophenol **25** to benzoxazol-2-one **26**,[20] more recently, a selenium-based catalyst has been used to perform this reaction (Scheme 6).[21] Recently, some of us reported that palladium(II) acetate $Pd(OAc)_2$ and 1,4-bis(diphenylphosphino)butane (dppb) catalyze the cyclocarbonylation of *o*-allyl phenol as well as *o*-allyl cardanol derivatives.[22] In this context, we report the cyclocarbonylation reaction of 5-*n*-pentadecyl-2-nitrophenol **6** carried out under mild conditions in the presence of the homogeneous catalytic system $Pd(OAc)_2$/dppb and a 1:1 mixture of CO/H_2 to produce the benzoxazol-2-one derivative **28** in good yield (85%) (Scheme 7). FTIR spectrum of 5-*n*-pentadecyl-2-nitrophenol **6** used as starting material shows characteristic bands centred at 1623, 1580, 1528 cm^{-1} (asymmetric stretch) and 1330 cm^{-1} (symmetric stretch) due to the NO_2 group. As expected, these signals are not present in the IR spectrum of the cyclocarbonylated product and a new strong peak characteristic of carbonyl compounds is found at 1742 cm^{-1}. In this reaction the formation of an isocyanate **27** as intermediate is presumed. The isocyanate **27** reacts further with the hydroxyl group to give the final product.



Scheme 6.



Scheme 7.

3. Conclusion

In the present paper we describe the reaction of 3-*n*-pentadecylphenol and 3-*n*-pentadecylphenol derivatives with nitric acid providing the corresponding nitro derivatives. The reaction occurred in mild conditions, with high yields and easy work-up procedures. The starting material with a long alkyl chain in *meta* position, not easily accessible directly by synthetic means, is a natural compound easily available from processing of cashew kernel (*A. occidentale* L.).

The nitro derivatives were processed with $MeReO_3$ and provided an interesting application of this oxidative system. One of these derivatives has been cyclocarbonylated to the corresponding benzoxazole-2-one in high yield.

4. Experimental

4.1. General

All solvents are ACS reagent grade and used without further purification. IRFT spectra were performed in Nujol mulls. Mass spectra EI were obtained at an ionizing voltage of 70 eV. ^{1}H NMR, ^{13}C NMR were recorded at 400 and 100 MHz, or 200 and 50 MHz, respectively, All NMR spectra were recorded in $CDCl_3$. Chemical shifts (δ_H) are reported in parts per million (ppm), relative to TMS as internal standard. All coupling constants (*J*) values are given in Hertz. Chemical shifts (δ_C) are reported in parts per million (ppm), relative to $CDCl_3$, as internal standard in a broad band decoupled mode. The abbreviations used are as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad. Gas-chromatography and mass spectrometry were performed by the use of HP5890 gas-chromatograph and by a Shimadzu GC–MS QP5050A spectrometer equipped with an Allthech® AT-20 column (0.25 mm, 30 m). TGA/DSC were carried out on a LABSYSTM TGA/DSC. Chromatographic purifications were performed on columns packed with Merck silica gel 60, 230–400 mesh for flash technique. Thin layer chromatography was carried out using Merck platen Kieselgel 60 F 25G. All new compounds showed satisfactory elemental analysis (C±0.35; H±0.30; N±0.30). Some overlaps in ^{13}C NMR of CH_2 resonances of long aliphatic chain occur.

4.1.1. General procedure for the nitration reactions. To a magnetically stirred solution of 3-*n*-pentadecylphenol **5** (1 mmol) in methanol (10 mL) a stoichiometric amount of nitric acid (65%) (1 mmol) in methanol (10 mL) was added dropwise over 30 min at room temperature. The reaction mixture was dried over anhydrous sodium sulfate, the solvent was evaporated under reduced pressure and then extracted with ethyl acetate (40 mL×3). The organic layer was washed with water and dried with sodium sulfate. After evaporation of the solvent, products **6–8** were separated by chromatography on a silica gel column (cyclohexane ethyl acetate mixtures) as oils.

The same procedure was used for preparation of products **14** and **15** from 5-*n*-pentadecyl-2-*tert*-butylphenol **13**.

For the synthesis of products **9–11**, **16** nitric acid (65%) (2 mmol) in methanol (20 mL) while for the synthesis of product **12** nitric acid (65%) (3 mmol) in methanol (30 mL) were used. The reactions can be carried out in acetonitrile and isolated reaction products can be crystallized from cyclohexane.

4.1.1.1. 5-*n*-Pentadecyl-2-nitrophenol 6. Bright yellow crystals. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.87 (3H, t, J=6.8 Hz, CH_3), 1.19–1.38 (24H, m, CH_2), 1.61 (2H, m, $ArCH_2CH_2$), 2.62 (2H, t, J=7.6 Hz, $ArCH_2$), 6.80 (1H, dd, J=8.8 Hz, 1.6 Hz, *H*-4), 6.94 (1H, d, J=1.6 Hz, *H*-6), 7.99 (1H, d, J=8.8 Hz, *H*-3), 10.61 (1H, s, *OH*). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.5, 23.1, 27.3, 29.6, 29.8, 29.9, 30.1, 30.8, 32.3, 36.4, 119.1, 120.9, 125.0, 131.8, 154.6, 155.2. IR ν_{max}(Nujol) 3623, 1623, 1580, 1330 cm^{-1}. EIMS: *m/z* (relative intensity) 349 (M$^+$, 10), 332 (42), 314 (100). Anal. Calcd for $C_{21}H_{35}NO_3$ (349.51): C, 72.17; H, 10.09; N, 4.01. Found C, 72.23; H, 10.22; N, 4.18%.

4.1.1.2. 3-*n*-Pentadecyl-4-nitrophenol 7. Brown solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.87 (3H, t, J=6.8 Hz, CH_3), 1.21–1.40 (24H, m, CH_2), 1.58–1.68 (2H, m, $ArCH_2CH_2$), 2.89 (2H, t, J=8.0 Hz, $ArCH_2$), 5.88 (1H, s, *OH*), 6.71–6.78 (2H, m, *Ar*), 7.97 (1H, d, J=9.6 Hz, *H*-5). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.1, 22.6, 29.5, 29.7, 30.4, 31.9, 33.8, 113.5, 118.0, 128.0, 141.9, 142.2, 159.6. IR ν_{max}(Nujol) 3382, 1615, 1597, 1513, 1324 cm^{-1}. EIMS: *m/z* (relative intensity) 349 (M$^+$, 32), 332 (15), 314 (100). Anal. Calcd for $C_{21}H_{35}NO_3$ (349.51): C, 72.17; H, 10.09; N, 4.01. Found C, 72.31; H, 10.24; N, 3.92%.

4.1.1.3. 3-*n*-Pentadecyl-2-nitrophenol 8. Brown solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.87 (3H, t, J=6.7 Hz, CH_3), 1.20–1.45 (24H, m, CH_2), 1.52–1.64 (2H, m, $ArCH_2CH_2$), 2.90 (2H, t, J=8.0 Hz, $ArCH_2$), 6.82 (1H, d, J=7.6 Hz, *H*-4), 6.98 (1H, dd, J=8.0 Hz, 1.2 Hz, *H*-6), 7.38 (1H, t, J=8.0 Hz, *H*-5), 9.94 (1H, s, *OH*). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.3, 22.9, 27.1, 29.6, 29.8, 29.9, 30.4, 30.8, 32.2, 34.7, 117.2, 123.0, 134.7, 135.5, 140.7, 154.5. IR ν_{max}(Nujol) 3190, 1609, 1589, 1533, 1345 cm^{-1}. EIMS: *m/z* (relative intensity) 349 (M$^+$, 15), 332 (35), 314 (100). Anal. Calcd for $C_{21}H_{35}NO_3$ (349.51): C, 72.17; H, 10.09; N, 4.01. Found C, 72.09; H, 10.21; N, 4.12%.

4.1.1.4. 5-*n*-Pentadecyl-2,4-dinitrophenol 9. White powder. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.88 (3H, t, J=7.5 Hz, CH_3), 1.21–1.39 (24H, m, CH_2), 1.58–169 (2H, m, $ArCH_2CH_2$), 2.99 (2H, t, J=8.0 Hz, $ArCH_2$), 7.13 (1H, s, *H*-6), 8.86 (1H, s, *H*-3), 10.79 (1H, s, *OH*). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.4, 22.9, 29.5, 29.6, 29.7, 29.8, 29.9, 30.4, 32.2, 34.0, 122.7, 123.6, 131.1, 141.5, 149.3, 157.2. IR ν_{max}(Nujol) 3294, 1633, 1582, 1540, 1342 cm^{-1}. EIMS: *m/z* (relative intensity) 394 (M$^+$, 12), 377 (100). Anal. Calcd for $C_{21}H_{34}N_2O_5$ (394.51): C, 63.93; H, 8.69; N, 7.10. Found C, 63.78; H, 8.79; N, 7.23%.

4.1.1.5. 3-*n*-Pentadecyl-2,4-dinitrophenol 10. White powder. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.87 (3H, t, J=6.6 Hz, CH_3), 1.17–1.35 (24H, m, CH_2), 1.58–1.65 (2H, m, $ArCH_2CH_2$), 2.98 (2H, t, J=8.0 Hz, $ArCH_2$), 6.96 (1H, d, J=9.2 Hz, *H*-6), 8.15 (1H, d, J=9.2 Hz, *H*-5), 10.88 (1H, s, *OH*). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.3, 22.9, 27.1, 29.6, 29.7, 29.9, 30.3, 32.1, 34.9, 121.1, 126.1, 132.5, 142.1, 145.4, 147.5. IR ν_{max}(Nujol) 3256, 1618, 1585, 1546, 1349 cm^{-1}. EIMS: *m/z* (relative intensity) 394 (M$^+$, 12), 377 (100). Anal. Calcd for $C_{21}H_{34}N_2O_5$ (394.51): C, 63.93; H, 8.69; N, 7.10. Found C, 63.75; H, 8.82; N, 7.21%.

4.1.1.6. 3-*n*-Pentadecyl-2,4,6-trinitrophenol 12. Deep brown solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.88 (3H, t, J=7.6 Hz, CH_3), 1.24–1.46 (24H, m, CH_2), 1.57–1.66 (2H, m, $ArCH_2CH_2$), 2.91 (2H, t, J=8.0 Hz, $ArCH_2$), 8.97 (1H, s, *H*-5), 11.12 (1H, s, *OH*). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.2, 22.8, 28.9, 29.2, 29.4, 29.6, 29.7, 29.9, 30.3, 32.0, 123.5, 131.2, 140.4, 140.6, 143.1, 149.5. IR ν_{max}(Nujol) 3273, 1635, 1593, 1536, 1356 cm^{-1}. EIMS: *m/z* (relative intensity) 440 (M$^+$, 56), 422 (15), 404 (100). Anal. Calcd for $C_{21}H_{33}N_3O_7$ (439.50): C, 57.39; H, 7.57; N, 9.56. Found C, 57.29; H, 7.65; N, 9.68%. TGA/DSC were carried out by controlled heating under a flow of dry air or nitrogen at a heating rate of 25 °C/min. Under a flow of dry air an enthalpy of −1074.91 and a total percentage weight lose of 36.5% was observed at 284 °C. Under a flow of nitrogen an enthalpy of −1169.35 and a total percentage weight lose of 32.3% was observed at 284 °C.

4.1.1.7. 2-*tert*-Butyl-5-*n*-pentadecyl-4-nitrophenol 14. White powder. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.87 (3H, t, J=7.2 Hz, CH_3), 1.18–1.36 (24H, m, CH_2), 1.41 (9H, s, $C(CH_3)_3$), 1.57–1.68 (2H, m, $ArCH_2CH_2$), 2.84 (2H, t, J=8.0 Hz, $ArCH_2$), 5.55 (1H, s, *OH*), 6.56 (1H, s, *H*-6), 7.99 (1H, s, *H*-3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.4, 22.9, 29.4, 29.6, 29.8, 29.9, 30.7, 32.1, 33.4, 34.7, 119.2, 125.6, 135.2, 139.1, 142.0, 158.3. IR ν_{max}(Nujol) 3326, 1629, 1582, 1496, 1335 cm^{-1}. EIMS: *m/z* (relative intensity) 405 (M$^+$, 2), 388 (45), 375 (22), 357 (5), 169 (100). Anal. Calcd for $C_{25}H_{43}NO_3$ (405.61): C, 74.03; H, 10.69; N, 3.45. Found C, 74.11; H, 10.79; N, 3.36%.

4.1.1.8. 3-*n*-Pentadecyl-6-*tert*-butyl-2-nitrophenol 15. White powder. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.89 (3H, t, J=7.4 Hz, CH_3), 1.18–1.36 (24H, m, CH_2), 1.43 (9H, s, $C(CH_3)_3$), 1.56–1.64 (2H, m, $ArCH_2CH_2$), 2.84 (2H, t, J=8.0 Hz, $ArCH_2$), 6.75 (1H, d, J=8.0 Hz, *H*-5), 7.39 (1H, d, J=8.0 Hz, *H*-4), 10.56 (1H, s, *OH*). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.1, 22.6, 29.2, 29.4, 29.6, 29.7, 30.5, 31.9, 34.4, 35.2, 122.0, 132.1, 136.2, 137.5, 138.2, 153.7. IR ν_{max}(Nujol) 3319, 1621, 1565, 1488, 1329 cm^{-1}. EIMS: *m/z* (relative intensity) 405 (M$^+$, 3), 388 (35), 375 (7), 169 (100). Anal. Calcd for $C_{25}H_{43}NO_3$ (405.61): C, 74.03; H, 10.69; N, 3.45. Found C, 74.16; H, 10.53; N, 3.36%.

4.1.1.9. 3-*n*-Pentadecyl-6-*tert*-butyl-2,4-dinitrophenol 16. White powder. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.87 (3H, t, J=7.5 Hz, CH_3), 1.20–1.35 (24H, m, CH_2), 1.44 (9H, s, $C(CH_3)_3$), 1.64 (2H, m, $ArCH_2CH_2$), 2.89 (2H, t, J=8.0 Hz, $ArCH_2$), 7.92 (1H, s, *H*-5), 9.63 (1H, s, *OH*). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.6, 23.1, 28.8, 29.3, 29.4, 29.8, 29.9, 30.1, 30.3, 30.5, 32.3, 36.1, 127.8, 132.7, 137.9, 138.9, 143.1, 154.5. IR ν_{max}(Nujol) 3332, 1615, 1575, 1475, 1334 cm^{-1}. EIMS: *m/z* (relative intensity) 450 (M$^+$, 2), 435 (12), 434 (30), 433 (100). Anal. Calcd for $C_{25}H_{42}N_2O_5$ (450.61): C, 66.64; H, 9.39; N, 6.22. Found C, 66.55; H, 9.51; N, 6.30%.

4.1.2. General procedure for $MeReO_3$ oxidation of cardanol derivatives. To the suspension of the appropriate nitrocardanol derivative (1 mmol) and MTO (2% in weight) in acetic acid (1.0 mL) was added 35% hydrogen peroxide (ca. 8.0 mmol) in several batches. The reaction mixture was stirred at 80 °C under a nitrogen atmosphere for 4 days. The reaction was monitored by TLC (ethyl ester/ethyl acetate=9.5:0.5).

The reaction mixture was diluted with ethyl acetate (40 mL) and a small amount of MnO_2 was added to decompose the excess of H_2O_2. After filtration of MnO_2 the organic layer was washed with NaCl saturated solution (5 mL×3), dried with Na_2SO_4 and evaporated under reduced pressure. The products were obtained by chromatographic purification (cyclohexane ethyl acetate mixtures) and identified by spectroscopic analyses, mass spectroscopy and comparison with authentic samples.

4.1.2.1. *O*-Pentadecanoyl-5-*n*-pentadecyl-2-nitrophenol 17. Yellow oil. ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.92 (6H, m, CH_3), 1.23–1.65 (50H, m, CH_2), 2.49–2.60 (2H, m, CO–CH_2), 2.91–3.05 (2H, m, $ArCH_2$), 6.80 (1H, d, J=10.0 Hz, *H*-4), 6.92 (1H, s, *H*-6), 8.0 (1H, d, J=10.0 Hz, *H*-3). ^{13}C NMR (50 MHz, $CDCl_3$): δ 14.1, 14.3, 22.5, 22.7, 25.0, 29.0, 29.3, 29.4, 29.5, 29.7, 31.9, 32.1, 32.5, 33.7, 35.8, 124.7, 125.3, 128.5, 139.2, 147.2, 148.0, 168.9. EIMS: *m/z* (relative intensity) 573 (M$^+$, 100), 558 (25), 544 (39), 376 (43), 348 (55). Anal. Calcd for $C_{36}H_{63}NO_4$ (573.88): C, 75.34; H, 11.06; N, 2.44. Found C, 75.37; H, 11.10; N, 2.39%.

4.1.2.2. *O*-Pentadecanoyl-3-*n*-pentadecyl-4-nitrophenol 21. Yellow oil. ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.93 (6H, m, CH_3), 1.23–1.75 (50H, m, CH_2), 2.31–2.46 (2H, m, CO–CH_2), 2.84–2.99 (2H, m, $ArCH_2$), 6.71 (1H, s, *H*-2), 6.74 (1H, d, J=8.5 Hz, *H*-6), 7.97 (1H, d, J=8.5 Hz, *H*-5). ^{13}C NMR (50 MHz, $CDCl_3$): δ 14.2, 22.5, 22.7, 25.0, 29.0, 29.3, 29.4, 29.5, 29.6, 29.7, 29.8, 31.8, 31.9, 32.6, 33.5, 121.1, 121.9, 126.3, 132.7, 147.2, 156.7, 171.8. EIMS: *m/z* (relative intensity) 573 (M$^+$, 100), 558 (21), 544 (31), 376 (48), 348 (49). Anal. Calcd for $C_{36}H_{63}NO_4$ (573.88): C, 75.34; H, 11.06; N, 2.44. Found C, 75.38; H, 11.13; N, 2.38%.

4.1.2.3. *O*-Pentadecanoyl-3-*n*-pentadecyl-2-nitrophenol 22. Yellow oil. ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.80–0.92 (6H, m, CH_3), 1.23–1.70 (50H, m, CH_2), 2.24–2.38 (2H, m, CO–CH_2), 2.80–2.96 (2H, m, $ArCH_2$), 6.77–6.84 (1H, m, *Ar*), 6.86–6.95 (1H, m, *Ar*), 7.26–7.35 (1H, m, *Ar*). ^{13}C NMR (50 MHz, $CDCl_3$): δ 14.1, 14.3, 22.7, 25.0, 29.0, 29.3, 29.4, 29.5, 29.6, 29.7, 31.8, 31.9, 32.6, 33.7, 118.2, 129.3, 132.7, 132.9, 143.0, 147.2, 168.9. EIMS: *m/z* (relative intensity) 573 (M$^+$, 100), 558 (21), 544 (55), 530 (45), 376 (48), 348 (37). Anal. Calcd for $C_{36}H_{63}NO_4$ (573.88): C, 75.36; H, 11.06; N, 2.44. Found C, 75.39; H, 11.12; N, 2.34%.

4.1.2.4. *para*-Benzoquinone 23. Yellow oil. ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.75–0.87 (3H, m, CH_3), 1.15–1.34 (24H, m, CH_2), 1.28(9H, s, $C(CH_3)_3$), 1.45–1.68 (2H, m, $ArCH_2CH_2$), 2.29–255 (2H, m, $ArCH_2$), 6.51–6.62 (1H, s, *Ar*). ^{13}C NMR (50 MHz, $CDCl_3$): δ 14.3, 22.7, 25.6, 29.0, 29.1, 29.3, 29.4, 29.5, 29.6, 29.8, 31.9, 35.8, 132.8, 147.1, 147.4, 160.6, 175.4, 177.7. EIMS: *m/z* (relative intensity) 419 (M^+, 100), 404 (71), 390 (46), 376 (41), 362 (39). Anal. Calcd for $C_{25}H_{41}NO_4$ (419.6): C, 71.56; H, 9.85; N, 3.34. Found C, 71.60; H, 9.79; N, 3.41%.

4.1.2.5. *para*-Hydroquinone 24. Yellow oil. ^1H NMR (200 MHz, $CDCl_3$): δ 0.82–0.95 (3H, m, CH_3), 1.18–1.35 (24H, m, CH_2), 1.37 (9H, s, $C(CH_3)_3$), 1.48–1.69 (2H, m, $ArCH_2CH_2$), 2.50–2.68 (2H, m, $ArCH_2$), 6.67 (1H, s, *Ar*). ^{13}C NMR (50 MHz, $CDCl_3$): δ 14.2, 22.7, 25.4, 29.3, 29.4, 29.5, 29.6, 29.8, 30.0, 30.3, 31.9, 33.3, 113.1, 116.1, 130.6, 137.4, 143.9, 148.8. EIMS: *m/z* (relative intensity) 421 (M^+, 100), 406 (63), 392 (51), 378 (48), 364 (37). Anal. Calcd for $C_{25}H_{43}NO_4$ (421.6): C, 71.22; H, 10.28; N, 3.32. Found C, 71.24; H, 10.21; N, 3.39%

4.1.3. Procedure for the cyclocarbonylation reaction. Palladium(II) acetate (0.01 mmol) and dppb (0.04 mmol) were dissolved in of dry toluene (5 mL) and 5-*n*-pentadecyl-2-nitrophenol **6** (1 mmol) was added. The autoclave was purged three times with CO and pressurized with CO (300 psi) and H_2 (300 psi). The reaction mixture was heated with stirring for 24 h at 100 °C (oil bath temperature). The reaction mixture was cooled to room temperature, the solution was concentrated and the residue was extracted with ether. The benzoxazol-2-one **28** was purified by chromatography using petroleum ether and diethyl ether as eluant.

White solid. ^1H NMR (200 MHz, $CDCl_3$): δ 0.88 (3H, t, J=6.5 Hz, CH_3), 1.15–2.30 (26H, m, CH_2), 2.63 (2H, t, J=7.5 Hz, $ArCH_2$), 7.03 (1H, s, *Ar*), 7.25–8.00, (2H, m, *Ar*). ^{13}C NMR (50 MHz, $CDCl_3$): δ 14.5, 23.1, 29.6, 29.8, 29.9, 30.0, 30.1, 32.2, 32.4, 36.3, 110.1, 124.1, 129.2, 131.1, 132.3, 144.6, 157.0. IR ν_{max}(Nujol) 3277, 1742, 1498, 1255, 1170 cm^{-1}. EIMS: *m/z* (relative intensity) 345 (M^+, 59), 317 (7), 162 (12), 148 (100). Anal. Calcd for $C_{22}H_{35}NO_2$ (345.52): C, 76.47; H, 10.21; N, 4.05. Found C, 76.61; H, 10.32; N, 3.92%.

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