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The silver nitrate oxidation of 2,2,4,6,7-pentamethylcoumaran-5-ol

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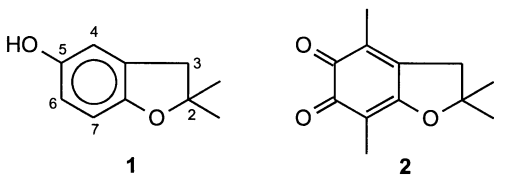
Abstract—The silver nitrate oxidation of 2,2,4,6,7-pentamethylcoumaran-5-ol (**1**) was investigated. The complex mixture of products received is in partial disagreement with the mechanisms supposed so far and proposes a less strong Mills–Nixon effect than assumed until now. Consecutive reactions of 2,2,4,7-tetramethylcoumaran-5,6-dione (**2**), which was received as main product, were examined. © 2002 Elsevier Science Ltd. All rights reserved.

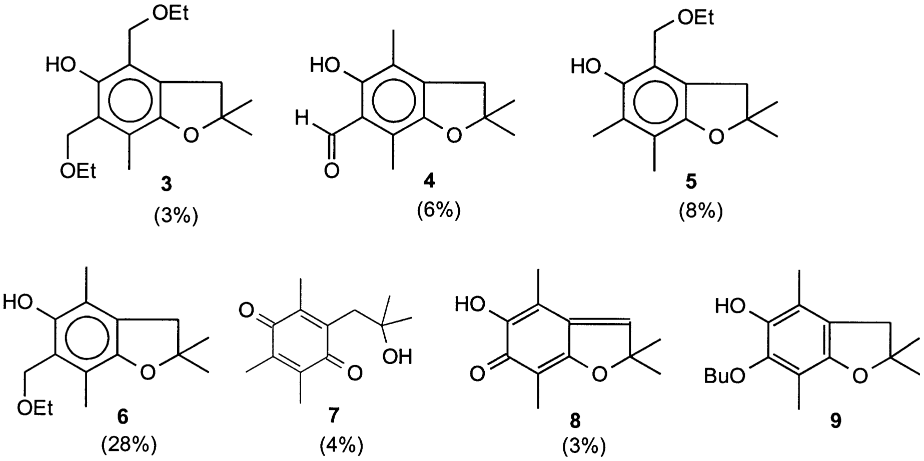
1. Introduction

We recently reported on the oxidation reactions of 2,2,4,6,7-pentamethylcoumaran-5-ol (**1**),[1] where we mentioned the formation of 2,2,4,7-tetramethylcoumaran-5,6-dione (**2**) as a result of the oxidation of **1** with silver nitrate (Scheme 1). Compound **1** has often been looked at as being the coumaran analog of the α-tocopherol model compound 2,2,5,7,8-pentamethylchroman-6-ol exceeding the latter in antioxidant activity.[2]



Scheme 1.

The further investigation of the above-mentioned reaction is caused by two ongoing discussions. So, the directing ability of the dihydrofuran ring leading to reactions in 6-position[3,4] of the aromatic ring exclusively and the dihydropyran ring leading to reactions in 5-position[5] has been widely and controversially discussed as Mills–Nixon effect. Moreover,



Scheme 2.

Keywords: silver nitrate; oxidation; coumaran derivatives; *o*-quinone; phosphole.

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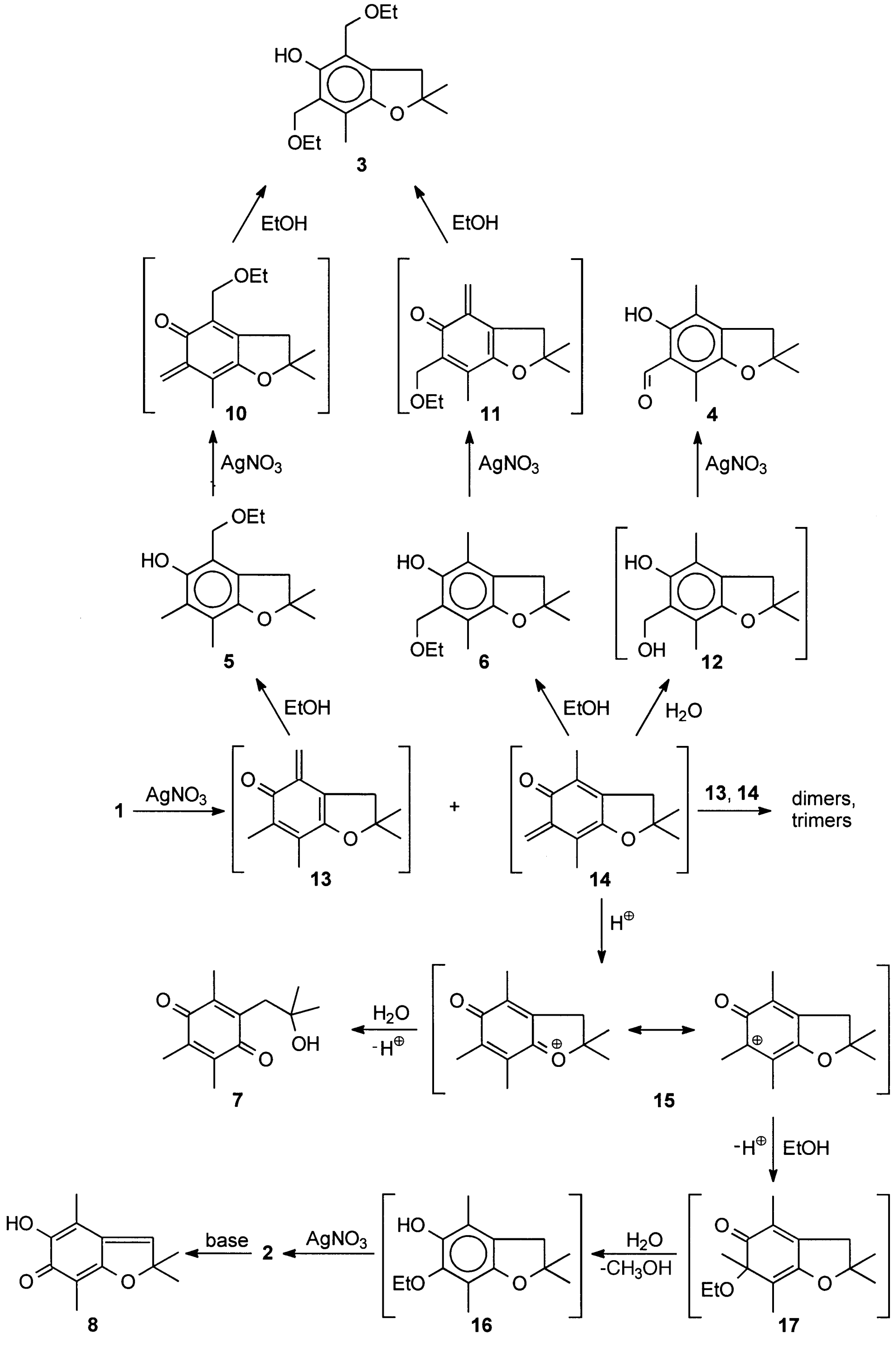
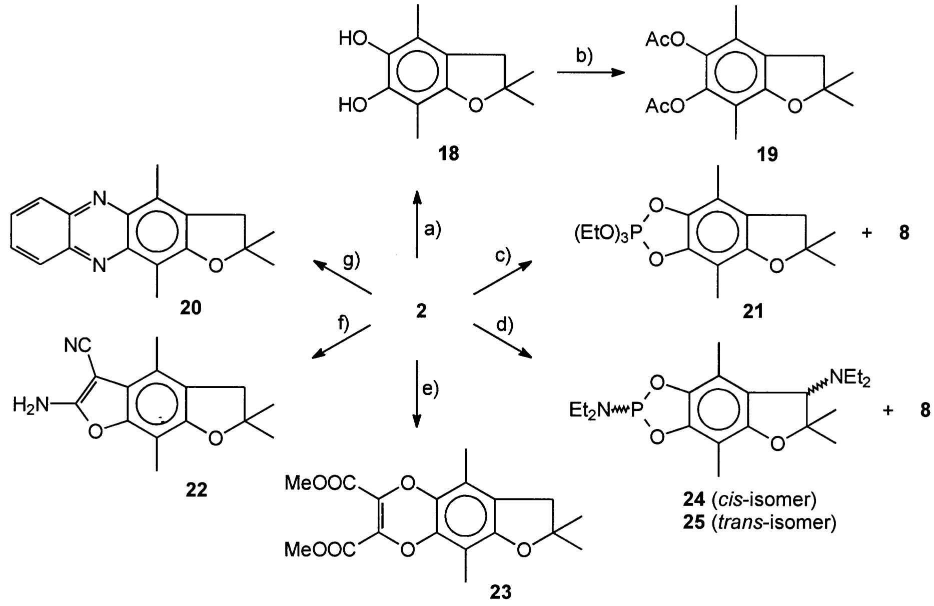


Scheme 3.

there have been contradictory opinions concerning the mechanism of the oxidation of α-tocopherol and 2,2,5,7,8-pentamethylchroman-6-ol to the corresponding *o*-quinones. Southwell-Keely et al. plead for a way involving the formation of an *o*-quinone methide with subsequent addition of water and release of formaldehyde.[6,7] Rosenau et al. suggest the formation of a *p*-quinoid structure the isomeric form of which does add the solvent alcohol in 5-position.[8] After elimination of methanol and further oxidation the formation of the *o*-quinone is observed. The silver nitrate oxidation of coumaran-5-ols has not been dealt with so far.[9]

2. Results and discussion

In the reaction of **1** with silver nitrate **2** is formed and could be isolated as red needles in 40% yield.[1] The remaining oil was shown to consist of six major fractions along with some minor fractions which could not yet be identified. The upper four major fractions were found to be compounds **3–8** (Scheme 2). The lower two were a mixture of several dimeric and trimeric compounds. The pattern of their mass spectra were consistent with those given by Dean and Orabi[3] for the oxidation of **1** with potassium



Scheme 4. (a) **2**, Zn-powder, glacial acetic acid, 90°C, 10 min; (b) **2**, acetic anhydride, sodium acetate, 84% (overall yield); (c) **2**, triethyl phosphite, THF_{dry}, r.t., Ar, 4 h, **8** 8%, **21** 82%; (d) **2**, tris(diethyl)aminophosphine, THF_{dry}, r.t., Ar, 4 h, **8** 25%, **24** 35%, **25** 35%; (e) **2**, dimethyl acetylenedicarboxylate, r.t., 3 d, 16%; (f) **2**, methanol/glacial acetic acid (3:1), malononitrile, Et_2NH, r.t., 2 d, 22%; (g) **2**, *o*-phenylendiamine, glacial acetic acid, 90°C, 2 h, 89%.

hexacyanoferrate in toluene and those found by us for the oxidation of **1** with silver oxide in *n*-hexane. R_f-values and HPLC data were the same as well.

To investigate the oxidation in more detail the reaction was then carried out in *n*-butanol (*n*-butanol proved to be inert under the reaction conditions applied and was considered prior to ethanol with regard to purity and detectibility of the expected products) and the evolving gases were passed into $CDCl_3$. When analyzed by NMR and MS spectroscopy the formation of methanol could be shown while none of the other products discussed in the literature (formaldehyde, formic acid, CO_2) were found. With GC-MS a product was detected the mass spectra of which {[*m/z*, (%)]: 265 (2, M^+), 264 (19, M), 218 (100), 138 (43), 109 (10), 59 (20)} could give evidence for the existence of 6-butoxy-2,2,4,7-tetramethylcoumaran-5-ol (**9**, Scheme 2). Furthermore, we recorded pH-values during the reaction course. Immediately after the addition of silver nitrate to the ethanolic solution of **1** the pH-value drops below 2 and stays at this level during the whole reaction. As the evolution of nitric gases was observed after some time it can be anticipated that with traces of water (the solvent was used without drying) nitric acid is formed. The reaction of **1** with Ag^+-ions to the radical cation which can deliver a proton as proposed by Suarna et al.[7] could contribute as well to the sudden decrease of the pH-value.

If we assume that the mechanism will not differ in principal in the oxidation of the coumaran-5-ol and the chroman-6-ol system our data raise some questions. The existence of compounds **3**–**6** as well as the formation of the dimers and trimers can hardly be explained without anticipating an intermediate *o*-quinone methide. On the other hand the occurrence of methanol and of compounds **7** and **9** cannot be coped with in this way. We would suggest the reaction to proceed in the following way (Scheme 3). In the first step the two *o*-quinone methides **13** and **14** are formed. They can add further *o*-quinone methide to give the observed dimers and trimers in a Diels–Alder reaction, the solvent ethanol to form the 4- and the 6-ethoxymethyl compounds **5** and **6**, water to yield the 6-hydroxymethyl compound **12** or a proton to give mesomer **15**. The latter can either react with water to yield the *p*-quinone **7**[1] by α-cleavage or add ethanol to form the cyclohexadienon **17**. The latter can eliminate the 4a-methyl group as methanol, for instance after protonation of the carbonyl group and nucleophilic attack of water at C-4a, thus forming the pyrocatechol derivative **16**. This reaction could well be driven by the possibility of rearomatization. Compound **16** should finally be oxidized with excess silver nitrate to *o*-quinone **2**. Aldehyde **4** could be formed by oxidation of **12**. Compounds **3** and **8** are obviously secondary products. Compound **3** will be derived from either **5** or **6** or both through oxidation to the *o*-quinone methides **10** and **11** and subsequent addition of ethanol. Isomer **8** is quantitatively received if **2** is treated with traces of base and is formed in traces if **2** is left standing in air.

The action of a Mills–Nixon effect can be supported to the point that a clear preference as to substitution in 6-position is perceivable but the reaction does not take place in this position exclusively.[‡] A problem still remaining is the role of the NO_3^- without which the reaction does not proceed in this way.

o-Quinone **2** can undergo a variety of further reactions. In the presence of bases **2** is converted into the isomer **8**. So **8** is formed quantitatively when **2** is stirred in chloroform with catalytic amounts of *N*-methylpiperidine while **2** remains unchanged if stirred in ethanol.

[‡] A similar behaviour with less strict Mills–Nixon effects was observed for reactions of 2-methyl-3-phenyl-4,6,7-trimethylcoumaran-5-ol and 2,5,7,8-tetramethylchroman-6-ol-2-carboxylic acid (unpublished results, in preparation).

The reduction of **2** to the pyrocatechol **18** is fully reversible in air and **18** can be trapped with acetic anhydride to give the diacetate **19** (Scheme 4). The reaction of **2** with *o*-phenylenediamine in acetic acid gives the phenazine **20** in good yield. The cycloaddition of **2** with dimethyl acetylenedicarboxylate forms the adduct **23**.

While **2** under basic conditions in most cases forms **8** as the main product there are some exceptions. In the reaction of **2** with triethyl phosphite benzodioxaphosphole **21** is obtained in 82% yield[§] along with 8% of isomer **8** only. The ^{31}P NMR signal has quite a large upfield shift (−48.6) which in other cases was attributed to the influence of the phosphole ring.[10,11] Reaction of **2** with tris(diethyl)aminophosphine gives a 1:1 mixture of the diastereomers **24** and **25**[§] and the isomer **8**. Obviously, compounds **24** and **25** were not formed from the *o*-quinone **2** directly but via the isomer **8**. Reaction of **2** with malononitrile forms the benzofuran **22** in rather poor yield.

3. Experimental

3.1. General methods

Melting points were received with a Kofler–Boetius apparatus and are corrected. ^{1}H NMR, ^{13}C NMR, ^{31}P NMR, and 2D NMR spectra (NOESY, COSY, HSQC, HMBC) were recorded either on a Bruker AC-200P or on a Bruker DRX-500 spectrometer. Spectra were taken in $CDCl_3$ and are reported in parts per million downfield from TMS as internal standard. IR spectra were determined on a Nicolet 205 and UV spectra on a Varian cary 3 spectrometer. Electron impact mass spectra were done at 70 eV on a Hewlett–Packard 589/II spectrometer, for GC-MS a Hewlett–Packard device (GC: HP 5890/II, capillary DB-5 MS, helium (0.75 mL min^{-1}), injection on column; MS: HP 5972, EI, 70 eV) was used. Elemental analysis was determined on a CHN-S analyser (Carlo Erba). Analytical TLC was performed using Merck prepared plates (silica gel 60 F-254 on aluminium). Merck silica gel (63–200 μm) was used for chromatography.

3.1.1. Oxidation of 1. Compound **1** (1.00 g, 4.85 mmol) was heated in absolute ethanol (50 mL) to 70°C and was treated under stirring with carefully pulverized $AgNO_3$ (3.8 g, 22.0 mmol). The reaction mixture was heated under reflux for 20 min during which time the colour of the solution changed to blood red, silver precipitated and the evolution of nitric gases was observed. After cooling and filtering water (30 mL) was added to the filtrate and the mixture was extracted with CH_2Cl_2 (3×30 mL). The organic layer was washed twice with little cold water and dried (Na_2SO_4). After evaporation of the solvent there remained a red oil from which 0.40 g (40%) 2,2,4,7-tetramethylcoumaran-5,6-dione (**2**) precipitated as purple needles. They were filtrated and washed with little cold ether. The washings were evaporated and together with the remaining oil chromatographed on silica gel (*n*-pentane/ethyl acetate 10:1). The major bands listed in order of appearance could be identified, as the following products (the substitution pattern of all compounds was determined with 2D NMR spectroscopy (NOESY, COSY, HSQC, HMBC)).

3.1.2. 5-Hydroxy-2,2,4,7-tetramethylcoumaran-5-ol-6-carbaldehyde (4). R_f-value 0.69; bright yellow needles from *n*-pentane; yield 0.06 g (6%); mp 85°C; ^{1}H NMR ($CDCl_3$, 500.13 MHz): δ=1.45 (s, 6H), 2.09 (s, 3H), 2.37 (s, 3H), 2.94 (s, 2H), 10.16 (s, 1H), 12.12 (s, 1H); ^{13}C NMR ($CDCl_3$, 125.8 MHz): δ=10.0; 11.7; 28.3; 43.3; 85.5; 116.6; 116.8; 120.4; 137.9; 149.4; 156.9; 194.6; NOESY spectra: strong cross coupling between aldehyde-H and H-7a protons; UV (methanol) λ_{max} 390 nm; IR (KBr) $\tilde{\nu}$ 3430, 2959, 1638, 1455, 1265 cm^{-1}; Anal. calcd for $C_{13}H_{16}O_3$: C, 70.89; H, 7.32. Found C, 70.75; H, 7.28.

From the fraction containing compounds **4** and **6** (equal R_f-values) the latter one precipitated after evaporating the major part of the solvent, while the former one remained in solution giving an oil after complete evaporation of the solvent.

3.1.3. 6-Ethoxymethyl-2,2,4,7-tetramethylcoumaran-5-ol (6). R_f-value 0.51; light yellow solid from *n*-pentane/ethyl acetate 3:1; yield 0.34 g (28%); mp 56°C; ^{1}H NMR ($CDCl_3$, 500.13 MHz): δ=1.27 (t, 3H, J=7.0 Hz), 1.44 (s, 6H), 2.08 (s, 3H), 2.09 (s, 3H), 2.91 (s, 2H), 3.60 (q, 2H, J=7.0 Hz), 4.70 (s, 2H), 7.63 (s, 1H); ^{13}C NMR ($CDCl_3$, 125.8 MHz): δ=11.3; 12.4; 15.1; 28.4; 42.8; 66.2; 68.2; 85.2; 113.6; 119.0; 119.3; 125.9; 148.2; 150.3; NOESY spectra: cross coupling between H-6a and H-7a; Anal. calcd for $C_{15}H_{22}O_3$: C, 71.97; H, 8.86. Found C, 72.14; H, 8.90.

3.1.4. 4-Ethoxymethyl-2,2,6,7-tetramethylcoumaran-5-ol (5). R_f-value 0.51; light brown oil; yield 0.10 g (8%); ^{1}H NMR ($CDCl_3$, 500.13 MHz): δ=1.27 (t, 3H, J=7.0 Hz), 1.44 (s, 6H), 2.08 (s, 3H), 2.13 (s, 3H), 2.88 (s, 2H), 3.59 (q, 2H, J=6.9 Hz), 4.58 (s, 2H), 7.34 (s, 1H); ^{13}C NMR ($CDCl_3$, 125.8 MHz): δ=11.5; 12.2; 15.8; 28.4; 42.2; 66.2; 69.3; 85.1; 115.5; 118.5; 120.7; 123.2; 147.6; 150.5; NOESY spectra: cross coupling between H-3 and H-4a; Anal. calcd for $C_{15}H_{22}O_3$: C, 71.97; H, 8.86. Found C, 72.14; H, 8.90.

3.1.5. 4,6-Diethoxymethyl-2,2,7-trimethylcoumaran-5-ol (3). R_f-value 0.39; yellow-brown oil; yield 0.04 g (3%); ^{1}H NMR ($CDCl_3$, 300.13 MHz): δ=1.23 (t, 6H, J=7.1 Hz), 1.42 (s, 6H), 2.13 (s, 3H), 2.94 (s, 2H), 3.56 (q, 4H, J=7.1 Hz), 4.54 (s, 2H), 4.62 (s, 2H), 7.67 (s, 1H); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ=11.6; 15.1; 15.2; 28.3; 42.4; 65.7; 65.8; 65.9; 67.2; 85.3; 117.6; 118.3; 121.3; 125.2; 148.6; 150.7; Anal. calcd for $C_{17}H_{26}O_4$: C, 69.36; H, 8.90. Found C, 69.62; H, 8.83.

3.1.6. 5-Hydroxy-2,2,4,7-tetramethyl-2*H*-benzofuran-6-one (8). R_f-value 0.36; bright yellow needles from *n*-pentane/ethyl acetate 5:1; yield 0.03 g (3%); mp 122°C; ^{1}H NMR ($CDCl_3$, 500.13 MHz): δ=1.47 (s, 6H), 1.86 (s, 3H), 2.00 (s, 3H), 6.81 (s, 1H), 7.32 (s, 1H); ^{13}C NMR ($CDCl_3$, 125.8 MHz): δ=7.4; 10.5; 25.4; 94.0; 104.0; 105.2; 131.4; 144.5; 146.8; 169.6; 181.5; NOESY spectra: strong cross coupling between H-3 and H-2a protons, weak

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[§] Estimated by NMR, compounds are not stable to purification and were analyzed via 2D NMR only.

cross coupling between H-3 and H-4a signals; UV (methanol) λ_{max} 314, 385 nm; IR (KBr) $\tilde{\nu}$ 3420, 2930, 1610 cm^{-1}; Anal. calcd for $C_{13}H_{18}O_2$: C, 69.88; H, 6.85. Found C, 70.06; H, 6.90.

3.1.7. 5-Acetyloxy-2,2,4,7-tetramethylcoumaran-6-yl acetate (19). 0.10 g (0.48 mmol) 2,2,4,7-tetramethylcoumaran-5,6-dione (**2**) were dissolved in 10 mL glacial acetic acid. 0.10 g zinc powder, 0.5 mL acetic anhydride and 0.02 g pulverized, water free sodium acetate were added and the mixture was warmed to 90°C for 10 min. The reaction was quenched with 10 mL water and extracted with 2×10 mL diethyl ether. The combined organic layers were washed ($NaHCO_3$, H_2O, NaCl) and dried (Na_2SO_4). The product was chromatographed on silica gel (*n*-pentane/ethyl acetate 4:1); yield 0.12 g (84%); yellow oil; ^{1}H NMR ($CDCl_3$, 300.13 MHz): δ=1.39 (s, 6H), 1.89 (s, 3H),1.91 (s, 3H), 2.20 (s, 3H), 2.21 (s, 3H), 2.84 (s, 2H);); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ=9.4; 13.1; 20.2; 28.5; 42.2; 86.8; 110.9, 123.1; 124.5, 134.0; 140.6, 154.8, 168.4; 169.0; Anal. calcd for $C_{16}H_{20}O_5$: C, 65.73; H, 6.90. Found C, 65.58; H, 6.92.

3.1.8. 2,2,4,11-Tetramethyl-2,3-dihydrofuro[2,3-*b*]phenazine (20). 0.21 g (1.00 mmol) 2,2,4,7-tetramethylcoumaran-5,6-dione (**2**) and 0.22 g (2.00 mmol) *o*-phenylendiamine were dissolved in 20 mL glacial acetic acid and kept for 2 h at 90°C. Then 20 mL water are added and the mixture was extracted three times with 20 mL diethyl ether. The etheric phases were washed ($NaHCO_3$, H_2O) and dried (Na_2SO_4). The product was purified on a silica gel column (*n*-pentane/ethyl acetate 2:1); bright yellow crystals; yield 0.25 g (89%); mp 128–130°C; ^{1}H NMR ($CDCl_3$, 300.13 MHz): δ=1.53 (s, 6H), 2.58 (s, 3H), 2.67 (s, 3H), 3.15 (s, 2H), 7.65 (m, 2H), 8.13 (dd, 2H, J=7.6, 2.4 Hz); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ=9.6; 14.0; 28.5; 42.5; 87.3; 127.9; 129.6; 129.0; 129.2; 130.2; 135.0; 140.0; Anal. calcd for $C_{18}H_{18}N_2O$: C, 77.66; H, 6.52; N 10.06. Found C, 77.42; H, 6.59; N 9.66.

3.1.9. 2,2,2-Triethoxy-4,6,6,8-tetramethyl-6,7-dihydro-2λ^5-furo[2,3-*f*][1,3,2]benzodioxaphosphole (21). In an argon atmosphere 0.17 g (1.00 mmol) freshly distilled triethylphosphite were added to a solution of 0.21 g (1 mmol) 2,2,4,7-tetramethylcoumaran-5,6-dione (**2**) in 20 mL dry THF. The mixture was stirred for 4 h at room temperature. During this time its original red colour changes to light brown. The solvent was evaporated in vacuo and the resulting brown oil was immediately examined on a NMR device. It contains 2,2,2-triethoxy-4,6,6,8-tetramethyl-6,7-dihydro-2λ^5-furo[2,3-*f*][1,3,2]benzodioxaphosphole (**21**, yield 82%) and 5-hydroxy-2,2,4,7-tetramethyl-2*H*-benzofuran-6-one (**8**, yield 8%); ^{1}H NMR ($CDCl_3$, 500.13 MHz): δ=1.21 (dt, 9H, J=7.0 Hz, $^4J_{PH}$=1.6 Hz), 1.40 (s, 6H), 2.06 (s, 3H), 2.08 (s, 3H), 2.82 (s, 2H), 3.98 (dq, 6H, J=5.8 Hz, $^3J_{PC}$=9.7 Hz); ^{13}C NMR ($CDCl_3$, 125.8 MHz): δ=8.6; 12.0; 15.9 (d, $^3J_{PC}$=8.0 Hz); 28.2; 41.9; 63.5 (d, $^2J_{PC}$=10.9 Hz); 85.3; 100.2 (d, $^3J_{PC}$= 14.5 Hz); 113.2 (d, $^3J_{PC}$=14.7 Hz); 114.5; 134.5 (d, $^2J_{PC}$= 3.8 Hz); 141.9 (d, $^2J_{PC}$=4.4 Hz); 150.8; ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ −48.6.

3.1.10. 2-Amino-4,6,6,8-tetramethyl-5,6-dihydrobenzo-[1,2-*b*;4,5-*b*′]difurano-3-nitrile (22). 0.25 g (1.21 mmol) 2,2,4,7-tetramethylcoumaran-5,6-dione (**2**) were dissolved in 30 mL of a 3:1 mixture of methanol and glacial acetic acid. Then 0.20 g (3.00 mmol) malononitrile and finally ten drops of diethyl amine were added. The reaction mixture was stirred for two days at room temperature. Reaction was quenched with 30 mL of water and extracted three times with methylene chloride. The combined organic phases were washed with water twice and dried (Na_2SO_4). The major part of the solvent was evaporated in vacuo and the precipitating crystals were filtrated. After evaporation of the filtrate a dark brown oil remained. It was chromatographed on silica gel (*n*-pentane/ethyl acetate 4:1). The first fraction contains unreacted malononitrile, from the second fraction **26** crystallizes; colourless crystals; yield 0.07 g (22%); mp 200°C; ^{1}H NMR ($CDCl_3$, 500.13 MHz): δ=1.46 (s, 6H), 2.18 (s, 3H), 2.37 (s, 3H), 2.94 (s, 2H), 5.03 (s_{br}, 2H); ^{13}C NMR ($CDCl_3$, 125.8 MHz): δ=8.3; 14.6; 28.4; 42.0; 64.9; 86.8; 101.0; 116.6; 117.0; 121.4; 122.4; 147.7; 153.7; 163.9; IR (KBr) $\tilde{\nu}$ 3340, 2980, 2310, 1650 cm^{-1}; GC-MS (70 eV): *m/z*, (%) 257 (17, $(M+1)^+$), 256 (100), 241 (9), 224 (26), 214 (15), 196 (5), 128 (7); Anal. calcd for $C_{15}H_{16}N_2O_2$: C, 70.29; H, 6.29; N 10.93. Found C, 69.92; H, 6.24; N 10.53.

3.1.11. 2,2,4,9-Tetramethyl-2,3-dihydro-1,5,8-trioxacyclopenta[*b*]naphthalene-6,7-dicarboxylic acid dimethylester (23). 0.30 g (1.50 mmol) 2,2,4,7-tetramethylcoumaran-5,6-dione (**2**) were dissolved in 20 mL acetylendicarboxylic acid dimethylester. The solution was stirred for three days at room temperature. Excess ester was evaporated in vacuo and the remaining yellowish oil was purified on a silica gel column (*n*-pentane/ethyl acetate 4:1); yield 0.08 g (16%); colourless crystals; mp 90°C; ^{1}H NMR ($CDCl_3$, 300.13 MHz): δ=1.41 (s, 6H), 2.08 (s, 3H), 2.20 (s, 3H), 2.89 (s, 2H), 3.75 (s, 3H), 3.79 (s, 3H); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ=12.3; 17.1; 28.4; 42.5; 52.0; 52.2; 87.4; 115.8; 122.7; 128.0; 132.5; 134.4; 159.0; 168.4; 169.1; GC-MS (70 eV): *m/z*, (%) 293 [9, $(M+1)^+-2\ C{=}O^{\oplus}$], 292 (49), 261 (100), 245 (92), 202 (59), 174 (22); Anal. calcd for $C_{18}H_{20}O_7$: C, 62.06; H, 5.79. Found C, 62.18; H, 5.82.

3.1.12. *cis*-N^2,N^2,N^7,N^7-Tetraethyl-4,6,6,8-tetramethyl-6,7-dihydrofuro[2,3-*f*][1,3,2]-benzodioxaphosphol-2,7-diamine (24). Synthesis from 0.21 g (1.00 mmol) 2,2,4,7-tetramethylcoumaran-5,6-dione (**2**) and 0.25 g (1.00 mmol) tris(diethylamino)phosphane as described above for **21**. After evaporation of the solvent the resulting oil was immediately examined on a NMR device. It contains *cis*-N^2,N^2,N^7,N^7-tetraethyl-4,6,6,8-tetramethyl-6,7-dihydrofuro-[2,3-*f*][1,3,2]benzodioxaphosphol-2,7-diamine (**24**, yield 35%), *trans*-N^2,N^2,N^7,N^7-tetraethyl-4,6,6,8-tetramethyl-6,7-dihydrofuro[2,3-*f*][1,3,2]benzodioxaphosphol-2,7-diamine (**25**, yield 35%) and 5-hydroxy-2,2,4,7-tetramethyl-2*H*-benzo-furan-6-on (**8**, yield 25%); ^{1}H NMR ($CDCl_3$, 500.13 MHz): δ=0.87 (m, 6H), 1.03 (t, 6H, J=7.1 Hz), 1.30 (s, 3H), 1.32 (s, 3H), 1.96 (s, 3H), 2.09 (s, 3H), 2.71 (m, 4H), 2.82 (m, 4H), 3.73 (s, 1H); ^{13}C NMR ($CDCl_3$, 125.8 MHz): δ=8.5; 12.4; 13.7; 15.0; 23.0; 28.1; 38.8; 47.6; 70.1 (d)[‖]; 88.9; 101.6; 115.5; 118.2; 138.1 (d)[‖]; 144.5 (d)[‖]; 151.4; ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ=149.3 (qui, J_{PH}=7.9 Hz).

[‖] Overlapping signals, J_{PC} not determined.

3.1.13. *trans*-N^2,N^2,N^7,N^7-Tetraethyl-4,6,6,8-tetramethyl-6,7-dihydrofuro[2,3-*f*][1,3,2]-benzodioxaphosphol-2,7-diamine (25). ^{1}H NMR ($CDCl_3$, 500.13 MHz): δ=0.87 (m, 6H), 1.03 (t, 6H, J=7.1 Hz), 1.29 (s, 3H), 1.31 (s, 3H), 1.95 (s, 3H), 2.07 (s, 3H), 2.71 (m, 4H), 2.82 (m, 4H), 3.74 (s, 1H); ^{13}C NMR ($CDCl_3$, 125.8 MHz): δ=8.5; 12.2; 13.7; 15.0; 22.9; 27.9; 38.3; 47.6; 70.2; 89.0; 101.6; 115.3; 117.7; 138.0 (d)$^{\|}$; 144.5 (d)$^{\|}$; 151.4; ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ=150.9 (qui, J_{PH}=7.9 Hz).

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