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Interaction of 3,5-di-*tert*-butyl-*o*-benzoquinone with secondary amines—a pathway to new sterically hindered *N*,*N*-disubstituted *o*-aminophenols

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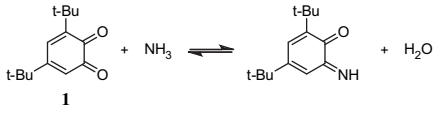
ABSTRACT

The interaction of 3,5-di-*tert*-butyl-*o*-benzoquinone with secondary amines has been studied. The synthetic procedure was developed in order to synthesize a series of new *N*,*N*-disubstituted *o*-aminophenols. The interaction of 3,5-di-*tert*-butyl-*o*-benzoquinone with dimethylamine leads to 2-(*N*,*N*-dimethylamino)-4,6-di-*tert*-butyl-phenol, which is oxidized in the reaction medium by the parent 3,5-di-*tert*-butyl-*o*-benzoquinone forming spirocompound 4,5′,6,7′-tetra-*tert*-butyl-3′-methyl-3′*H*-spiro[1,3-benzodioxol-2,2′-[1,3]benzoxazole].

1. Introduction

The chemistry of *o*-quinones is wide and interesting. For example, they can form chelate semiquinone or catecholate complexes with metals.[1] 3,5-Di-*tert*-butyl-*o*-benzoquinone (**1**) and its derivatives are widely used in coordination chemistry as spin labels or redox active ligands and their chemical properties have been previously studied. It is known that interaction of **1** withammonia leads to 2,4-di-*tert*-butyl-6-iminocyclohexa-2,4-dienone. This reaction is reversible and the equilibrium can be shifted toward *o*-iminoquinone by an excess of the ammonia (Scheme 1).[2]

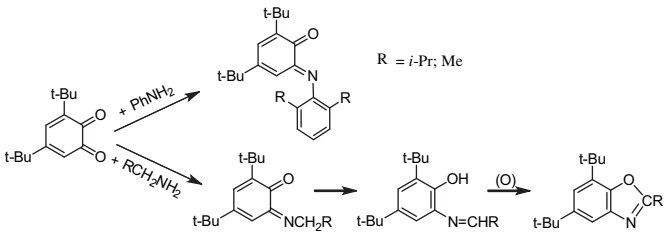


1

Scheme 1.

3,5-Di-*tert*-butyl-*o*-benzoquinone **1** interacts with primary amines via the less hindered carbonyl group (1,2-addition) with subsequent water elimination. Formally, this process can be considered to be a condensation process, as in case of reaction of **1** with NH_3.

The condensation product depends on the nature of amine. Reaction of **1** with 2,6-disubstituted anilines leads to *o*-iminoquinones.[3] Interaction of **1** with aliphatic amines having α-methylene protons results in *o*-aminophenols. Benzoxazoles can be obtained by the reaction of **1** with amines of the type RCH_2NH_2[4,5] (Scheme 2).



Scheme 2.

2. Results and discussion

In this paper, we report a study of the interaction of **1** with secondary amines when primary addition products cannot be stabilized by water elimination. It was found that 3,5-di-*tert*-butyl-*o*-benzoquinone **1** interacts with the excess of secondary amines (dimethyl- and diethyl-amines). The main products are the corresponding *o*-aminophenols **2** and **3** (yields 65% and 50%, respectively) (Scheme 3).

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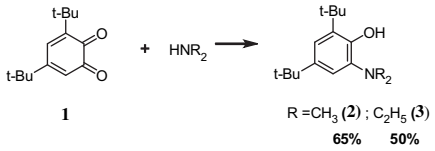
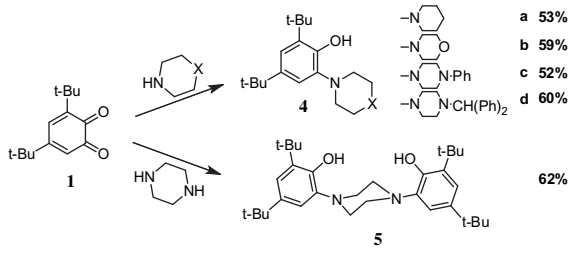


Scheme 3.

Using cyclic secondary amines (piperidine, morpholine, 1-phenylpiperazine, 1-(diphenylmethyl) piperazine) allow the synthesis of a number of new *o*-aminophenols **4**(**a**–**d**) under the same conditions. Bis-*o*-aminophenol **5** with a piperazine bridge was synthesized analogously (Scheme 4).



Scheme 4.

All *o*-aminophenols were isolated and characterized by IR-, NMR-spectroscopy and elemental analysis (see Experimental section, Fig. 1).

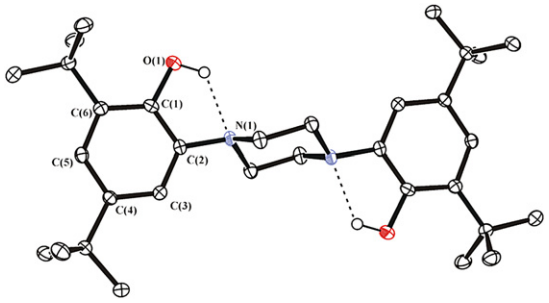
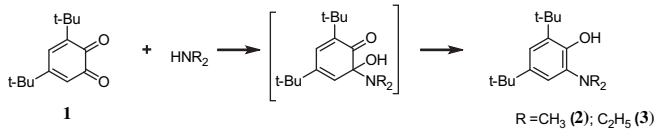


Fig. 1. The molecular structure of bis-*o*-aminophenol **5**. Bond lengths and angles are in the range as expected for comparable aromatic or cyclohexane systems, respectively.

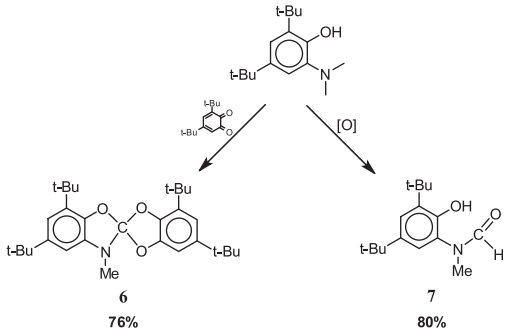
In order to explain the mechanism of transformation of the intermediate product of 1,2-addition into aminophenols we studied the interaction of **1** with dimethylamine thoroughly. The process was carried out at ambient temperature with a threefold excess of amine in dry methanol, acetonitryl, benzene, and heptane. The parent quinone conversion was monitored by TLC. Reaction occurs remarkably faster in the polar solvents: 2–3 h compared to 24 h in the case of benzene or heptane. Finally benzene or heptane reaction mixtures were refluxed with a Dean–Stark receiver. The amount of water in reaction mixtures has been measured in both cases. The water yield corresponds to a 60% yield of **2**. Consequently **2** is formed from the primary product of nucleophilic addition (cyclohexadienone) through the water elimination (Scheme 5).



Scheme 5.

Unfortunately our efforts to strictly identify reductant and structures of formed by-products were unsuccessful due to the presence of a wide variety of amine-derived by-products in the reaction mixture. This result conforms with previously published papers.[6] It seems that the most probable source of hydrogen is the excess of amine. This is confirmed by the fact that excess of amine is required for complete quinone disappearance. Quinone was not consumed during several days of reaction if an equimolar ratio of reagents was used.

The interaction of **1** with dimethylamine does not stop at the formation of **2**. Increasing the reaction temperature up to 50 °C leads to a decrease of yield of **2**. We have established two products of oxidation of **2**, which accumulated in the reaction mixture: spirocompound **6**—product of oxidation of **2** by parent *o*-quinone **1** and *N*-arylformamide **7**—product of oxidation of **2** by air (Scheme 6, Fig. 2).



Scheme 6.

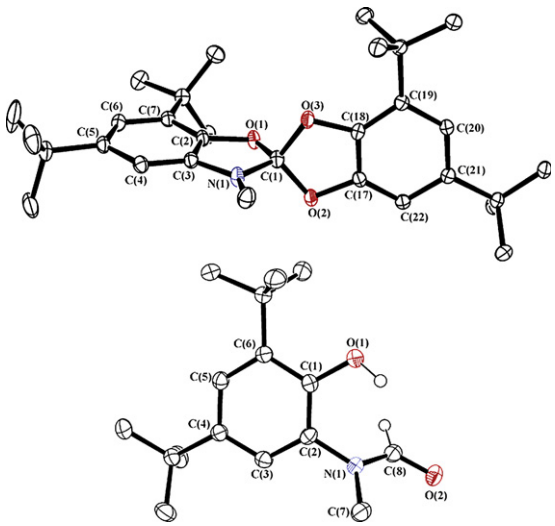
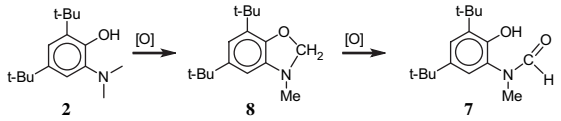


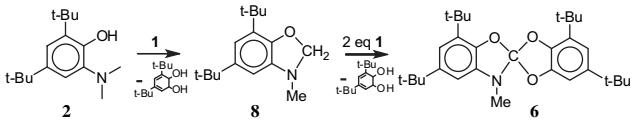
Fig. 2. The molecular structures of spirocompound **6** and *N*-methylformamide **7**. Bond lengths and angles are in the range as expected for comparable aromatic or spirocompound systems, respectively.

The *o*-aminophenol **2** was oxidized by PbO_2 and **1**, respectively, in order to prove the formation of **6** and **7** in the reaction mixture. After the treatment of **2** by PbO_2 followed by filtration from lead oxides, the reaction mixture was separated by column chromatography and two products were isolated: compound **7** and *N*-methyl-2,3-dihydrobenzooxazole (**8**). The latter is the primary product of *o*-aminophenol oxidation because it can be fully converted into **7** during prolonged oxidation by a fivefold excess of PbO_2 (Scheme 7). Formation of compounds of benzoxazole type as the products of interaction of **1** with primary aliphatic amines is known from literature.[5]



Scheme 7.

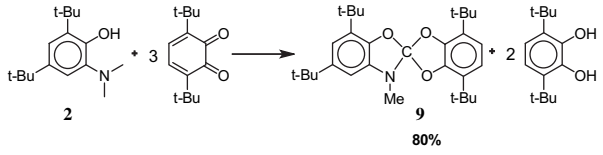
The quinonic colour of the solution disappears upon heating of a benzene solution of **1** with **2** (molar ratio 3:1) in an evacuated ampoule. Spirocompound **6** and 3,5-di-*tert*-butylcatechol (in 2:1 ratio) were detected by ^{1}H NMR as the products of the reaction (Scheme 8).



Scheme 8.

o-Quinone participates in both stages of the reaction: in the first step *o*-quinone **1** oxidizes **2** forming *N*-methyl-2,3-dihydrobenzooxazole **8**. The latter transforms quantitatively into **6** consuming 2 equiv of *o*-quinone **1**. Both reactions were monitored by ^{1}H NMR spectroscopy.

The oxidation of **2** by 3,6-di-*tert*-butyl-*o*-benzoquinone was carried out under similar conditions (Scheme 9) in order to evaluate the possibility of using the aforementioned reaction for the synthesis of similar structures. The product of this reaction **9** was isolated in 80% yield. It differs from **6** by the positions of the *tert*-butyl group in catecholate part of the molecule.



Scheme 9.

3. Conclusion

A convenient procedure for the synthesis of sterically hindered *o*-aminophenols via the interaction of 3,5-di-*tert*-butyl-*o*-benzoquinone with secondary amines has been developed.

It is significant that 2-(*N*,*N*-dimethylamino)-4,6-di-*tert*-butylphenol **2** can be oxidized into various products. The product nature depends on the oxidant used: formamide is a main product of the oxidation of **2** by oxygen or PbO_2 while spirocompounds are formed in the reaction of **2** with *o*-benzoquinones. This method can be used for a synthesis of various substituted formamides and spirocompounds.

4. Experimental section

4.1. General

3,5-Di-*tert*-butyl-*o*-benzoquinone (**1**) was prepared according to previously described procedures.[7] Solvents were purified by standard methods.[8]

The NMR spectra were recorded on a 'Bruker Avance DPX-200' spectrometer (200 MHz—^{1}H, 50 MHz—^{13}C) using $CDCl_3$ as the solvent and tetramethylsilane as the internal standard. IR-spectra were recorded by 'Specord M-80. Elemental analyses were obtained on 'EuroEA-3028-HT'. X-ray structure analyses were carried out on 'SmartApex' diffractometer (BrukerAXS). The H atoms were found from Fourier syntheses and refined isotropically. The structure was solved by direct method and refined on F^2 using SHELXTL package.[9] CCDC-772232 (**5**), 772231 (**7**), 772230 (**6**) contains the supplementary crystallographic data, which can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk.

4.2. All *N*,*N*-disubstituted *o*-aminophenols were synthesized using the single general procedure

A solution of 3,5-di-*tert*-butyl-*o*-benzoquinone (2.2 g; 0.01 mol) in MeOH (50 mL) and three-fold excess of dried amine was stirred at room temperature. When the cherry-red solution turned colorless *o*-aminophenol was formed. Upon concentration of the reaction mixture to 15–20 mL colorless crystals was collected by filtration and dried.

*4.2.1. 2-(N,N-Dimethylamino)-4,6-di-tert-butylphenol (**2**).* Colorless crystals, yield: 1.62 g (65%); mp=43–44 °C. Found (%): C, 77.09; H, 10.95. Calculated for $C_{16}H_{27}NO$ (%): C, 77.06; H, 10.91. IR (Nujol, ν/cm^{-1}): 3240br, 1610m, 1435s, 1365s, 1320s, 1275m, 1250s, 1205m, 1190s, 1160w, 1140w, 1115w, 1096w, 1045w, 970s, 875m, 855w, 815w, 785w, 770m, 740w, 700m, 650w, 630w, 535w, 455w. ^{1}H NMR ($CDCl_3$, δ/ppm, *J*/Hz): 1.30 and 1.41 (both s, 9H, *t*-Bu); 2.64 (s, 6H, N–CH_3); 7.08 (d, 1H$_{arom}$, *J*=2.3); 7.11 (d, 1H$_{arom}$, *J*=2.3); 7.70 (br s, 1H, OH). ^{13}C NMR ($CDCl_3$, δ/ppm): 29.6 and 31.9 (C(CH_3)$_3$); 34.7 and 35.1 (*C*(CH_3)$_3$); 45.6 (CH (N–CH_3)); 115.0 and 120.5 (CH, C(3 and 5)); 133.4 and 141.1 (*C*-*t*-Bu); 141.1 (*C*–N–CH_3); 148.0 (C–O).

*4.2.2. 2-(N,N-Diethylamino)-4,6-di-tert-butylphenol (**3**).* Colorless crystals, yield: 1.38 g (50%); mp=22 °C. Found (%): C, 77.89; H, 11.25. Calculated for $C_{18}H_{31}NO$ (%): C, 77.92; H, 11.26. IR (Nujol, ν/cm^{-1}): 3260 br, 1620s, 1490s, 1455s, 1425s, 1410m, 1400s, 1365m, 1345w, 1310m, 1300m, 1270m, 1255s, 1230s, 1210m, 1185w, 1150w, 1140w, 1090w, 955w, 875w, 815w, 775m, 730w, 690w. ^{1}H NMR ($CDCl_3$, δ/ppm, *J*/Hz): 0.96 (t, 6H, CH_3, *J*=7.2); 1.28 and 1.40 (both s, 9H, *t*-Bu); 2.90 (q, 4H, N–CH_2, *J*=7.2); 6.99 (d, 1H$_{arom}$, *J*=2.3); 7.09 (d, 1H$_{arom}$, *J*=2.3); 8.05 (s, 1H, OH). ^{13}C NMR ($CDCl_3$, δ/ppm): 13.0 (CH (CH_2-*C*H_3)); 29.5 and 31.8 (C(*C*H_3)$_3$); 34.5 and 34.7 (*C*(CH_3)$_3$); 49.8 (CH (N–CH_2)); 116.8 and 120.2 (CH, C(3 and 5)); 133.4 and 140.7 (*C*-*t*-Bu); 135.9 (*C*–N–CH_2); 150.0 (C=O).

*4.2.3. 2-(Piperidin-1-yl)-4,6-di-tert-butylphenol (**4a**).* Colorless crystals, yield: 1.53 g (53%); mp=82 °C. Found (%): C, 78.95; H, 10.81. Calculated for $C_{19}H_{31}NO$ (%): C, 78.84; H, 10.79. IR (Nujol, ν/cm^{-1}): 3260 br, 1610w, 1480s, 1425m, 1395m, 1365m, 1325w, 1290w, 1275w, 1250s, 1220m, 1205m, 1150w, 1120w, 1105w, 1065w, 1055w, 1030w, 970m, 865w, 810w, 770m, 735w, 675w, 650w, 630w. ^{1}H NMR ($CDCl_3$, δ/ppm, *J*/Hz): 1.29 and 1.41 (both s, 9H, *t*-Bu); 1.64–1.79 (m, 6H, CH_2); 2.72–2.86 (m, 4H, N–CH_2); 7.04 (d, 1H$_{arom}$, *J*=2.3); 7.10 (d, 1H$_{arom}$, *J*=2.3); 7.85 (br s, 1H, OH). ^{13}C NMR ($CDCl_3$, δ/ppm): 24.0 (CH_2); 27.0 (CH_2); 29.5 and 31.7 (C(CH_3)$_3$); 34.6 and 34.9 (*C*(CH_3)$_3$); 54.2 (CH (N–CH_2)); 115.5 and 120.2 (CH, C(3 and 5)); 133.8 and 140.8 (*C*-t-Bu); 139.7 (*C*–N–CH_2); 147.6 (C–O).

*4.2.4. 2-Morpholino-4,6-di-tert-butylphenol (**4b**).* Colorless crystals, yield: 1.72 g (59%); mp=143–145 °C. Found (%): C, 74.21; H, 10.01. Calculated for $C_{19}H_{31}NO$ (%): C, 74.18; H, 10.03. IR (Nujol, ν/cm^{-1}): 3215 br, 1610w, 1600w, 1425s, 1320m, 1300m, 1280s, 1260s, 1225m, 1210s, 1160m, 1150m, 1120s, 1065m, 1020w, 980m, 920w, 910w, 860m, 815w, 780w, 770m, 730m, 720m, 650w, 630w, 540w. ^{1}H NMR ($CDCl_3$, δ/ppm, *J*/Hz): 1.30 and 1.41 (both s, 9H, *t*-Bu); 2.88 (t, 4H, N–CH_2); 3.87 (t, 4H, O–CH_2); 7.08 (d, 1H$_{arom}$, *J*=2.2); 7.15 (d,

1H$_{arom}$, J=2.2); 7.67 (s, 1H, OH). ^{13}C NMR (CDCl$_3$, δ/ppm): 29.5 and 31.7(C(*C*H$_3$)$_3$); 34.6 and 35.0 (*C*(CH$_3$)$_3$); 53.1 (CH (N–CH$_2$)); 67.8 (CH (O–CH$_2$)); 115.6 and 120.9 (CH, C(3 and 5)); 134.4 and 141.3 (*C*-*t*-Bu); 138.0 (*C*–N–CH$_2$); 147.7 (C–O).

*4.2.5. 2-(4-Phenylpiperazin-1-yl)-4,6-di-tert-butylphenol (**4c**).* Colorless crystals, yield: 1.90 g (52%); mp=112 °C. Found (%): C, 78.60; H, 9.36. Calculated for $C_{24}H_{34}N_2O$ (%): C, 78.64; H, 9.35. IR (Nujol, ν/cm^{-1}): 3250 br, 1610s, 1510m, 1500m, 1425s, 1400m, 1385m, 1370m, 1325m, 1295w, 1250s, 1240s, 1210m, 1160w, 1145m, 1105w, 1065w, 990m, 985s, 920m, 875w, 820w, 790w, 765s, 690m, 650w, 635w, 520w. ^{1}H NMR (CDCl$_3$, δ/ppm): 1.30 and 1.42 (both s, 9H, *t*-Bu); 3.03–3.07 (m, 4H, C–N–C*H*$_2$); 3.36 (m, 4H, C*H*$_2$–N–Ph); 6.89–6.99 (m, 4H, *m*-, *p*-Ph, H(5)); 7.26–7.35 (m, 2H, *o*-Ph); 7.69 (s, 1H, OH). ^{13}C NMR (CDCl$_3$, δ/ppm): 29.5 and 31.7 (C(*C*H$_3$)$_3$); 34.6 and 35.0 (*C*(CH$_3$)$_3$); 50.4 and 52.8 (N–CH$_2$); 115.6; 116.5; 120.2; 120.9; 129.2; 134.3; 138.1; 141.3; 147.7; 151.3.

*4.2.6. 2-(N-Diphenylmethyl-piperazin-1-yl)-4,6-di-tert-butylphenol (**4d**).* Colorless crystals, yield: 2.74 g (60%); mp=155–156 °C. Found (%): C, 81.53; H, 8.83. Calculated for $C_{31}H_{40}N_2O$ (%): C, 81.49; H, 8.85. IR (Nujol, ν/cm^{-1}): 3230 br, 1610w, 1430m, 1395m, 1365s, 1350m, 1340m, 1315m, 1285s, 1270m, 1255s, 1225m, 1210m, 1185w, 1170w, 1135s, 1080m, 1010m, 990s, 960m, 930m, 880w, 850m, 820w, 785w, 770m, 755s, 750m, 700s, 695s, 650m, 630w, 590w, 520w. ^{1}H NMR (CDCl$_3$, δ/ppm, J/Hz): 1.31 and 1.41 (both s, 18H, t-Bu); 2.58 (br m, 4H, C*H*$_2$NCH); 2.91 (m, 4H, C*H*$_2$NC); 4.32 (s, 1H, NC*H*Ph$_2$); 7.147.48 (m, 10H (Ph) and 2H$_{arom}$); 7.77 (br s, 1H, OH). ^{13}C NMR, DEPT (CDCl$_3$, δ/ppm): 29.5 and 31.7 (C(*C*H$_3$)$_3$); 34.6 and 34.9 (*C*(CH$_3$)$_3$); 52.9 and 53.1 (NCH$_2$); 115.8 and 120.7 (CH, C(3 and 5)); 127.1 (CH, *p*-Ph); 128.0 and 128.6 (CH, *o*-, *m*-Ph); 134.0 and 141.0 (*C*-*t*-Bu); 138.3 (C–N); 142.6 (*C*HPh$_2$); 147.8 (C–O).

*4.2.7. 6,6'-(Piperazine-1,4-diyl)bis(2,4-di-tert-butylphenol) (**5**).* Colorless crystals, yield: 1.53 g (62%); mp=287–288 °C. Found (%): C, 77.70; H, 10.21. Calculated for $C_{32}H_{50}N_2O_2$ (%): C, 77.68; H, 10.19. IR (Nujol, ν/cm^{-1}): 3250 br, 1615w, 1425s, 1400m, 1365m, 1325m, 1285m, 1270m, 1245s, 1220m, 1200m, 1160m, 1130m, 1120m, 1075m, 950w, 895w, 870w, 845w, 815m, 790w, 765m, 740w, 680m, 410w. ^{1}H NMR (CDCl$_3$, δ/ppm, J/Hz): 1.33 and 1.43 (both s, 18H, *t*-Bu); 3.07 (m, 8H, CH$_2$), 7.15 and 7.18 (both d, 1H$_{arom}$, J=2.3); 7.69 (br s, 1H, OH). ^{13}C NMR, DEPT (CDCl$_3$, δ/ppm): 29.5 and 31.7 (C(*C*H$_3$)$_3$); 34.6 and 35.0 (*C*(CH$_3$)$_3$); 53.6 (CH$_2$); 115.5 and 120.9 (CH, C(3 and 5)); 134.3 and 141.2 (*C*-*t*-Bu); 138.1 (C–N); 147.7 (C–O). The crystals of **6** (CCDC-772232) suitable for X-ray structure determination were obtained by recrystallization from MeOH. Crystal data: $C_{32}H_{50}N_2O_2$, M=494.74, monoclinic, space group C2/C, Z=4 in a cell of dimensions: a=17.2309(1), b=8.8066(7), c=19.4719 (1) Å, α=90°, β=94.511(2)°, γ=90°, V=2945.6(4) Å^3, T=100(2) K, μ=0.068 mm^{-1}, d_{cal}=1.116 g/cm^3, 9618 reflections were measured, 3373 unique (R_{int}=0.0249), which were used in all calculations. $R_1[I>2\sigma(I)]$=0.0438, wR_2=0.1181, GOF(F^2)=1.030.

4.3. General procedure for preparation of spirocompounds 6 and 9

A solution of o-aminophenol **2** (2.5 g; 0.01 mol) and three-fold excess of 3,5- or 3,6-di-*tert*-butyl-*o*-benzoquinone (6.6 g; 0.03 mol) in benzene (50 mL) was refluxed until *o*-quinone color disappeared. Benzene was replaced by CH$_3$CN. The resulting solution was filtered off. Upon cooling colorless crystals are formed.

*4.3.1. 4,5',6,7'-Tetra-tert-butyl-3'-methyl-3'H-spiro[1,3-benzodioxol-2,2'-[1,3]benzoxazole] (**6**).* Colorless crystals, yield: 3.54 g (76%); mp=159 °C. Found (%): C, 77.40; H, 9.35. Calculated for $C_{30}H_{43}NO_3$ (%): C, 77.38; H, 9.31. IR (Nujol, ν/cm^{-1}): 1615s, 1420s, 1310s, 1290m, 1275m, 1265m, 1240s, 1210m, 1200m, 1165s, 1130w, 1100w, 1020s, 1000s, 965m, 935w, 915w, 865m, 855w, 840w, 820w, 795w, 750w, 740w, 720s, 655w. ^{1}H NMR (CDCl$_3$, δ/ppm, J/Hz): 1.32, 1.33, 1.34, and 1.35 (all s, 9H, *t*-Bu); 2.97 (s, 3H, CH$_3$); 6.53 and 6.77 (both d, C(4'),(6')H, J=1.9); 6.88–6.90 (AB, 2H, C (5), (7)H, J=1.9). ^{13}C NMR (CDCl$_3$, δ/ppm): 27.0 (NCH$_3$); 29.5, 29.7, 31.9, 32.0 (C(*C*H$_3$)$_3$); 34.1, 34.3, 35.0, 35.1(*C*(CH$_3$)$_3$); 101.0 (CH); 103.9 (CH); 113.4 (CH); 115.6 (CH); 130.8 (C); 131.6 (C); 134.9 (C); 136.3 (C); 140.1 (C); 140.5 (C); 144.8 (C); 145.1 (C); 145.2 (C). The crystals of **7** (CCDC 772231) suitable for X-ray were obtained from CH$_3$CN. Crystal data: $C_{30}H_{43}NO_3$, M=465.65, monoclinic, space group P2(1)/*c*, Z=4 in a cell of dimensions: a=9.9571(5), b=22.3032(12), c=13.0620(7) Å, α=90°, β=109.7810(10)°, γ=90°, V=2729.6(2) Å^3, T=130(2) K, μ=0.072 mm^{-1}, d_{cal}=1.133 g/cm^3, 23421 reflections were measured, 5352 unique (R_{int}=0.0375), which were used in all calculations. $R_1[I>2\sigma(I)]$=0.0502, wR_2=0.1251, GOF(F^2)=1.036.

*4.3.2. 4,5',7,7'-Tetra-tert-butyl-3'-methyl-3'H-spiro[1,3-benzodioxol-2,2'-[1,3]benzoxazole] (**9**).* Colorless microcrystalline powder, yield: 3.73 g (80%); mp=187–188 °C. Found (%): C, 77.41; H, 9.30. Calculated for $C_{30}H_{43}NO_3$ (%): C, 77.38; H, 9.31. IR (Nujol, ν/cm^{-1}): 1620m, 1510m, 1490s, 1425s, 1400m, 1370s, 1310s, 1265m, 1245s, 1210m, 1155s, 1130m, 1030s, 1000s, 970m, 890w, 845w, 810m, 795m, 740m, 655w, 640w. ^{1}H NMR (CDCl$_3$, δ/ppm, J/Hz): 1.33 and 1.34 (both s, 9H, *t*-Bu); 1.36 (s, 18H, *t*-Bu); 2.99 (s, 3H, CH$_3$); 6.56 and 6.78 (both d, C(4'),(6')H, J=1.8); 6.83 (s, 2H, C (5), (6)H). ^{13}C NMR (CDCl$_3$, δ/ppm): 27.5 (NCH$_3$); 29.3 (C (4), (7), C(*C*H$_3$)$_3$); 29.4 and 31.9 (C (5'), (7'), C(*C*H$_3$)$_3$); 33.7, 34.0, 34.9 (*C*(CH$_3$)$_3$); 100.9 (CH); 113.2 (CH); 118.3 (CH); 130.3 (C); 130.6 (C); 134.7 (C); 135.5 (C); 140.0 (C); 142.7 (C); 145.0 (C).

*4.3.3. N-(3,5-Di-tert-butyl-2-hydroxyphenyl)-N-methylformamide (**7**).* o-Aminophenol **2** (2.5 g, 0.01 mol) was dissolved in ether (40 mL) and PbO$_2$ was added (4.8 g, 0.02 mol). The reaction mixture was stirred at 20 °C for 1 h and then filtered. The ether was evaporated and residue was separated by column chromatography (silicagel 'Acros' 0.060–0.200 mm; eluent hexane/ethylacetate is 50:1). Two products were isolated.

From the *first fraction* 5,7-*di-tert-butyl*-3-*methyl*-2,3-*dihydrobenzo*[*d*]*oxazole* (**8**)was extracted. ^{1}H NMR (CDCl$_3$, δ/ppm, J/Hz): 1.30 and 1.35 (both s, 9H, *t*-Bu); 2.74 (s, 3H, CH$_3$); 5.17 (s, 2H, CH$_2$); 6.51 and 6.70 (both d, 1H$_{arom}$, J=1.8). ^{13}C NMR, DEPT (CDCl$_3$, δ/ppm): 29.7 and 31.9 (C(*C*H$_3$)$_3$); 34.2 and 34.9 (*C*(CH$_3$)$_3$); 35.2 (NCH$_3$); 90.8 (CH$_2$); 104.2 (CH); 114.4 (CH); 131.1 (C); 140.6 (C); 144.2 (C); 146.5 (C). After adding excess of PbO$_2$ to the solution of dihydrobenzoxazole **8** in ether its quantitative gives *N*-methylformamide **7**.

Then the *second fraction* was collected and the eluent was evaporated and residue was crystallized in ether. After being filtered colorless crystals of **7** washed with cold pentane and dried (mp=173–174 °C.) Found (%): C, 73.00; H, 9.55. Calculated for $C_{16}H_{25}NO_2$ (%): C, 72.96; H, 9.57. IR (Nujol, ν/cm^{-1}): 3320s, 1670s, 1590m, 1270w, 1250s, 1210m, 1185m, 1140w, 1120w, 1035m, 1020w, 920w, 875w, 825w, 810w, 775w, 745w, 720m, 660w, 640w. ^{1}H NMR (CDCl$_3$, δ/ppm, J/Hz) *isomer* **1**: 1.29 and 1.43 (both s, 9H, *t*-Bu); 3.21 (s, 3H, CH$_3$); 5.92 (br s, 1H, OH); 6.92 and 7.33 (both d, 1H$_{arom}$, J=1.8); 8.18 (s, 1H, H–C=O). *Isomer* **2**: 1.29 and 1.43 (both s, 9H, *t*-Bu); 3.45 (s, 3H, CH$_3$); 6.67 (s, 1H, OH); 7.00 and 7.29 (both d, 1H$_{arom}$, J=1.8); 8.31 (s, 1H, H–C=O). Ratio of isomers 2:1. ^{13}C NMR, DEPT (CDCl$_3$, δ/ppm): 29.6 and 31.5 (C(*C*H$_3$)$_3$); 29.9 (NCH$_3$); 34.3 and 35.3 (*C*(CH$_3$)$_3$); 122.4 (CH); 124.5 (CH); 128.4 (C); 137.6 (C); 142.8 (C); 148.8 (C); 164.6 (CH). Event of the barrier to internal rotation about the N–CO bond was discussed.[10] The crystals of **7** (CCDC 772230) suitable for X-ray structure determination were obtained from ether. There is one independent molecule of **7** in the unit cell. Disorders in molecule of **7** are absent. Therefore, only one type of rotamers exists in crystal of **7**. Crystal data: $C_{16}H_{25}NO_2$, M=263.37, triclinic, space group P–1, Z=2 in a cell of dimensions: a=6.0017(7), b=9.7281(11), c=14.3535(16) Å, α=70.565(2)°,

β=86.834(2)°, γ=75.457(2) °, V=764.59(15) Å^3, T=100(2) K, μ=0.074 mm^{-1}, d_{cal}=1.144 g/cm^3, 4249 reflections were measured, 2687 unique (R_{int}=0.0222), which were used in all calculations. $R_1[I>2\sigma(I)]$=0.0466, wR_2=0.1189, GOF(F^2)=1.034.

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Supplementary data

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.tet.2010.11.030.

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