Oxidation of 2-dialkylaminomethyl-4,6-di-*tert*-butylphenols

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Oxidative transformations of 2-dialkylaminomethyl-4,6-di-*tert*-butylphenols depend on the nature of the oxidant, the character of the substituents at the nitrogen atom, and the medium. A mechanism of the oxidation of these compounds is suggested. The molecular structure of the compound obtained as a result of oxidative trimerization of 2-dimethylaminomethyl-4,6-di-*tert*-butylphenol was established by X-ray structural analysis.

Key words: oxidation, 2-dialkylaminomethyl-4,6-di-*tert*-butylphenols, 3,5-di-*tert*-butylsalicylaldehyde; liquid-phase and solid-phase oxidative, heterocyclization.

We used oxidation of α-substituted derivatives of 2-methyl-4,6-di-*tert*-butylphenol in our development of methods for the synthesis of 3,5-di-*tert*-butylsalicylaldehyde (**1**). It was demonstrated that 2-hydroxymethyl-4,6-di-*tert*-butylphenol can be converted to aldehyde **1** in virtually quantitative yield.[1] Compound **1** was also formed in the oxidation of 2-dialkylaminomethyl-4,6-di-*tert*-butylphenols. However, the selectivity of this reaction was substantially lower, and products of dedialkylaminomethylation and oxidative heterocyclization were formed along with compound **1**. We studied oxidation in the series of 2-dimethylaminomethyl-, 2-morpholinomethyl-, and 2-dicyclohexylaminomethyl-4,6-di-*tert*-butylphenols (**2a—c**) under the action of $Mn(OAc)_3$ and PbO_2 in AcOH and C_6H_6, as well as in the absence of a solvent (in the solid phase). It was established that the direction of the oxidative transformation depends substantially on the character of the substituents at the nitrogen atom, the nature of the oxidant, and the medium. The structures of the resulting compounds (Table 1) provide evidence that one- and two-electron oxidation of compounds **2a—c** can occur to form radical intermediates, which are then converted by disproportionation, recombination, and fragmentation. In all the cases under study, aldehyde **1** was formed, which is reasonably attributable to one-electron oxidation of compounds **2a—c** followed by disproportionation of aroxyl radicals and solvolysis of quinonemethides (Scheme 1).

The mechanism under consideration gives steric reasons to accounts for the decrease in the yield of aldehyde **1** in the series **2a** > **2b** > **2c**, which corresponds to the decrease in the probability of disproportionation of $ArO^{\bullet}$. This mechanism also explains why the yield of aldehyde **1** in solid-phase reactions is greater than in liquid-phase reactions. On the other hand, the probability of fragmentation of $ArOH^{\bullet +}$ with elimination of $CH_2N^+R_2$ should increase in the series **2a—c**, which was confirmed experimentally. Fragmentation of com-

Table 1. Oxidation of 2-dialkylaminomethyl-4,6-di-*tert*-butylphenols

Oxidized substrate	Oxidant	Medium	Reaction products and yields (%)
2a	$Mn(OAc)_3 \cdot 2H_2O$	AcOH	**1** (31) + **6** (69)
	$Mn(OAc)_3 \cdot 2H_2O$	Solid phase	**1** (40) + **6** (60)
	$Mn(OAc)_3 \cdot 2H_2O$ + + $Mn(OAc)_2 \cdot 4H_2O$	AcOH	**1** (86) + **7** (14)
	PbO_2	C_6H_6	**1** (20) + **4** (80)
	PbO_2	Solid phase	**1** (40) + **4** (60)
2b	PbO_2	C_6H_6	**1** (21) + **5** (70) + + **3** (~9)
	PbO_2	Solid phase	**1** (~30) + **5** (~65) + + **3** (~5)
2c	$Mn(OAc)_3 \cdot 2H_2O$	AcOH, solid phase	**1** (<5) + **3** (>95)

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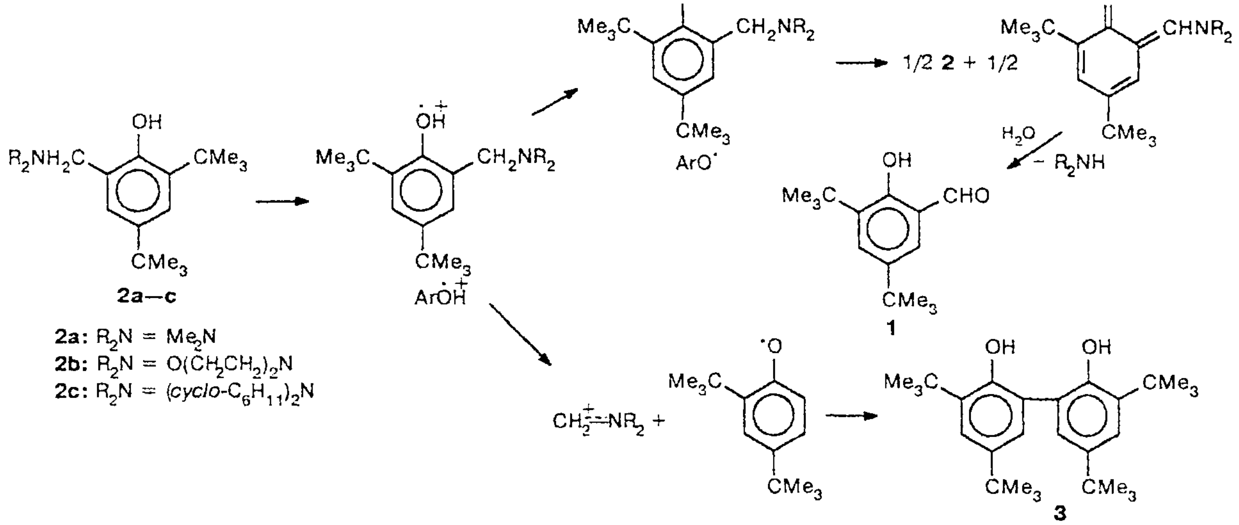
Scheme 1

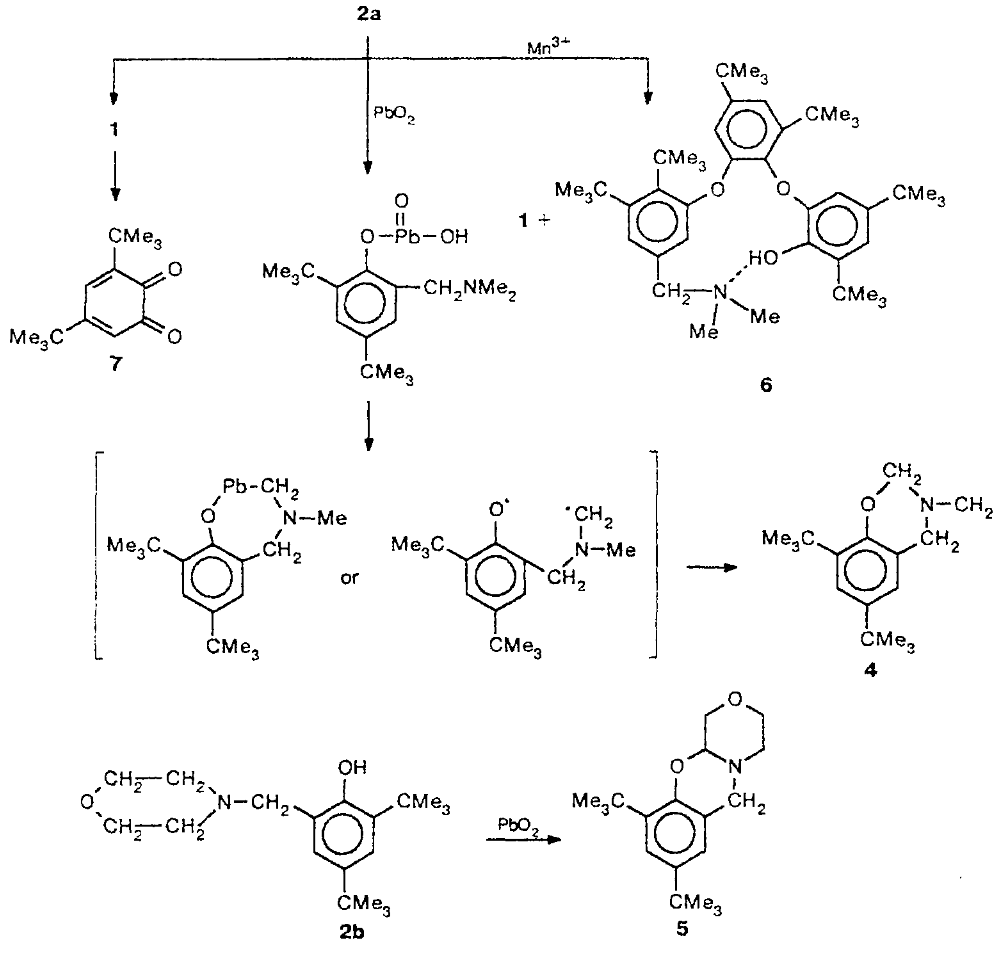


pound **2c** was the predominant process, giving a high yield of bisphenol **3**.

Products of oxidative heterocyclization **4** and **5** were formed as a result of two-electron oxidation of **2a** and **2b** (Scheme 2) with possible formation of Pb compounds or biradical particles as intermediates.

Therefore, it is necessary to use a two-electron oxidant (PbO$_2$) in the target synthesis of such heterocyclic

Scheme 2



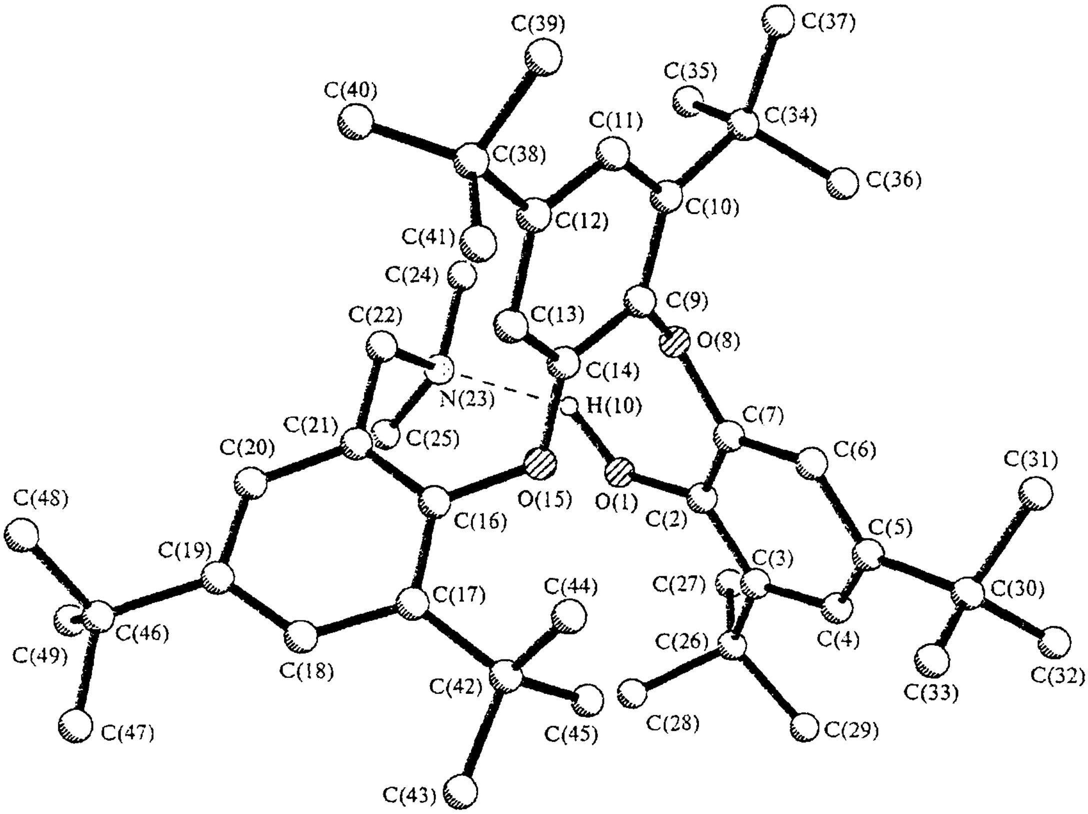


Fig. 1. Structure of compound **6**.

compounds. This was best confirmed by oxidation of compound **2a**: different results were obtained with the use of PbO_2 and $Mn(OAc)_3$. Heterocycle **4** was formed only under the action of PbO_2.

Oxidative trimerization of compound **2a** with the formation of product **6** is of particular interest. The structure of **6** was confirmed by spectral studies and X-ray structural analysis (Figs. 1 and 2). In product **6**, a macrocycle containing four heteroatoms is formed through an intramolecular hydrogen bond between the hydroxyl proton and the nitrogen atom of the dimethylamino group. When crystallized, compound **6** forms stable solvates in which a solvent molecule is located between two molecules of **6**. Apparently, coordination of the oxidant (Mn^{+3}) and molecule **2a** as a bidentate ligand plays a decisive role in the formation of product **6**. This was confirmed by a special experiment that demonstrated that an excess of a competitive complex-forming agent, $Mn(OAc)_2$, prevents the formation of product **6**. In the **2a**—Mn^{+3}—Mn^{+2} system (1 : 1.5 : 5), only aldehyde **1** was formed, which was then partially converted to 3,5-di-*tert*-butyl-*o*-benzoquinone (**7**).

Therefore, oxidation of 2-dialkylaminomethyl-4,6-di-*tert*-butylphenols opens up various synthetic possibilities.

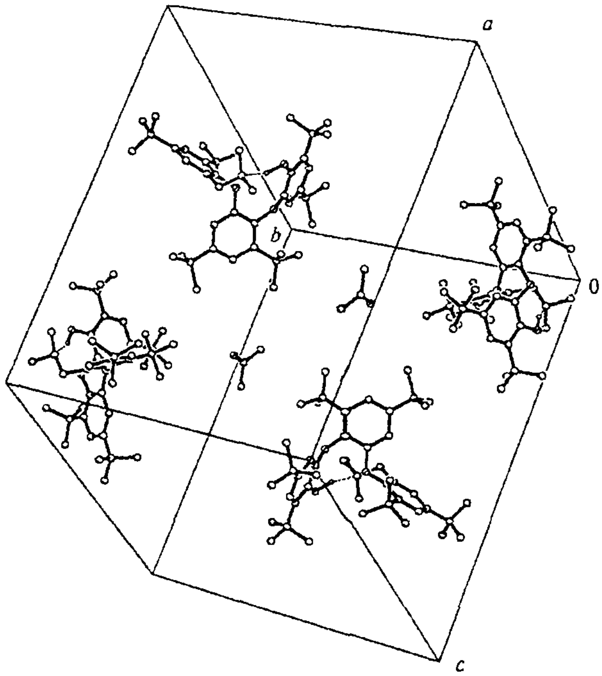


Fig. 2. Structure of the solvate of compound **6**.

Table 2 Coordinates ($\times 10^4$) and isotropic thermal parameters (equivalent thermal parameters for nondisordered atoms) ($U \times 10^2$/ Å^2) of nonhydrogen atoms in the structure of **6**

Atom	*x*	*y*	*z*	*U*
		Molecule **1**		
O(1)	2700(2)	−744(2)	7330(2)	67(1)
O(8)	2009(2)	−963(2)	8131(2)	50(1)
O(15)	2451(2)	−2158(2)	7995(2)	54(1)
N(23)	3713(3)	−1196(3)	8337(3)	67(2)
C(2)	2009(4)	−905(3)	7141(3)	48(2)
C(3)	1683(4)	−913(3)	6556(3)	56(2)
C(4)	997(4)	−1111(4)	6407(3)	62(2)
C(5)	647(3)	−1321(3)	6807(3)	54(2)
C(6)	981(4)	−1284(3)	7383(3)	52(2)
C(7)	1655(4)	−1075(3)	7554(3)	46(2)
C(9)	1962(3)	−1423(4)	8547(3)	49(2)
C(10)	1759(3)	−1258(4)	9044(3)	52(2)
C(11)	1819(4)	−1757(4)	9465(3)	65(2)
C(12)	2051(3)	−2380(4)	9410(3)	57(2)
C(13)	2252(3)	−2531(4)	8907(3)	57(2)
C(14)	2225(3)	−2045(4)	8490(3)	47(2)
C(16)	3003(4)	−2601(4)	8041(3)	53(2)
C(17)	2901(4)	−3180(4)	7717(3)	59(2)
C(18)	3470(4)	−3591(4)	7789(3)	68(2)
C(19)	4106(4)	−3452(4)	8142(4)	70(2)
C(20)	4178(4)	−2860(4)	8438(3)	68(2)
C(21)	3643(4)	−2415(4)	8397(3)	59(2)
C(22)	3746(4)	−1769(3)	8713(3)	62(2)
C(24)	3789(4)	−595(4)	8687(4)	100(3)
C(25)	4243(4)	−1215(5)	8008(4)	110(3)
C(26)	2049(4)	−704(5)	6084(3)	81(3)
C(27)	2352(5)	−23(5)	6209(4)	109(3)
C(28)	2625(5)	−1196(5)	6085(4)	106(3)
C(29)	1563(4)	−707(6)	5474(3)	128(4)
C(30)	−97(4)	−1572(4)	6610(3)	79(2)
C(31)	−526(6)	−1309(7)	7039(5)	102(4)
C(32)	−450(8)	−1337(8)	6017(7)	130(6)
C(33)	−85(8)	−2294(8)	6656(8)	140(6)
C(31A)	−562(13)	−1006(13)	6255(11)	68(8)
C(32A)	−123(12)	−2151(12)	6122(11)	72(7)
C(33A)	−343(15)	−1980(16)	7060(13)	101(10)
C(34)	1514(4)	−559(4)	9151(3)	72(2)
C(35)	2114(5)	−93(5)	9257(6)	170(6)
C(36)	972(6)	−322(5)	8635(4)	151(5)
C(37)	1202(8)	−538(5)	9661(5)	206(7)
C(38)	2094(4)	−2914(4)	9882(3)	80(3)
C(39)	1669(8)	−2676(8)	10324(7)	141(6)
C(40)	2819(7)	−3007(8)	10184(7)	125(5)
C(41)	1749(7)	−3529(6)	9609(5)	96(4)
C(39A)	2588(13)	−2659(12)	10476(10)	70(7)
C(40A)	2606(17)	−3539(16)	9801(14)	112(11)
C(41A)	1440(17)	−3115(18)	9987(16)	124(12)
C(42)	2212(4)	−3346(4)	7285(3)	65(2)
C(43)	2253(4)	−3990(4)	6966(4)	108(3)
C(44)	2013(4)	−2807(4)	6830(3)	91(3)
C(45)	1640(4)	−3431(4)	7614(4)	100(3)
C(46)	4733(5)	−3914(5)	8230(5)	97(3)
C(47)	4572(5)	−4507(5)	7845(5)	147(5)
C(48)	4952(7)	−4138(7)	8851(6)	193(7)
C(49)	5323(5)	−3539(5)	8082(6)	169(6)
		Molecule **2**		
O(1′)	2647(2)	−5500(2)	2414(2)	58(1)
O(8′)	1733(2)	−5284(2)	3049(2)	52(1)
O(15′)	2265(2)	−4093(2)	3022(2)	55(1)
N(23′)	3483(3)	−5048(3)	3451(2)	62(2)
C(2′)	1993(4)	−5316(3)	2131(3)	47(2)
C(3′)	1802(4)	−5276(3)	1528(3)	50(2)
C(4′)	1140(4)	−5058(3)	1270(3)	58(2)
C(5′)	686(3)	−4844(3)	1593(3)	55(2)
C(6′)	883(4)	−4909(3)	2188(3)	51(2)
C(7′)	1522(4)	−5141(3)	2449(3)	47(2)
C(9′)	1596(3)	−4810(4)	3435(3)	48(2)
C(10′)	1248(3)	−4984(4)	3856(3)	55(2)
C(11′)	1217(4)	−4497(4)	4264(3)	59(2)
C(12′)	1503(4)	−3881(4)	4275(3)	55(2)
C(13′)	1852(3)	−3734(3)	3855(3)	53(2)
C(14′)	1914(3)	−4206(4)	3446(3)	49(2)
C(16′)	2817(4)	−3647(4)	3154(3)	49(2)
C(17′)	2758(4)	−3061(4)	2837(3)	50(2)
C(18′)	3316(4)	−2642(3)	2990(3)	55(2)
C(19′)	3913(4)	−2779(3)	3420(3)	55(2)
C(20′)	3938(4)	−3384(4)	3701(3)	59(2)
C(21′)	3402(4)	−3828(4)	3568(3)	53(2)
C(22′)	3470(4)	−4496(4)	3852(3)	62(2)
C(24′)	4070(4)	−4987(5)	3189(4)	110(3)
C(25′)	3505(5)	−5673(4)	3759(4)	100(3)
C(26′)	2303(4)	−5481(4)	1160(3)	58(2)
C(27′)	2565(4)	−6177(4)	1301(3)	78(2)
C(28′)	1953(4)	−5456(4)	504(3)	93(3)
C(29′)	2909(4)	−4990(4)	1265(4)	92(3)
C(30′)	−28(4)	−4578(5)	1284(3)	83(3)
C(31′)	−134(8)	−3890(8)	1550(7)	76(5)
C(32′)	−228(11)	−4629(13)	683(9)	134(8)
C(33′)	−587(9)	−5035(9)	1524(8)	102(6)
C(31B)	68(9)	−4040(8)	778(7)	87(5)
C(32B)	−462(8)	−5103(8)	914(8)	89(5)
C(33B)	−364(10)	−4273(11)	1657(8)	113(7)
C(34′)	942(4)	−5668(4)	3883(3)	61(2)
C(35′)	394(4)	−5818(4)	3318(4)	92(3)
C(36′)	1504(5)	−6188(4)	3980(4)	95(3)
C(37′)	590(5)	−5729(5)	4391(4)	114(3)
C(38′)	1445(4)	−3370(4)	4725(3)	72(2)
C(39′)	1025(8)	−3589(7)	5133(6)	233(9)
C(40′)	2123(6)	−3214(7)	5089(6)	224(8)
C(41′)	1127(8)	−2752(6)	4437(5)	220(8)
C(42′)	2147(4)	−2904(4)	2335(3)	58(2)
C(43′)	2049(4)	−3445(4)	1868(3)	82(3)
C(44′)	1486(4)	−2822(4)	2549(3)	95(3)
C(45′)	2244(4)	−2256(4)	2028(3)	91(3)
C(46′)	4508(4)	−2276(4)	3601(4)	70(2)
C(47′)	5189(4)	−2635(4)	3649(4)	105(3)
C(48′)	4444(4)	−1723(4)	3157(4)	113(3)
C(49′)	4502(4)	−2004(5)	4200(4)	118(4)
O(1S)	89(14)	1974(11)	8953(15)	493(17)
C(1S)	868(24)	1935(29)	9275(27)	526(42)
C(2S)	608(28)	1452(17)	9525(15)	439(30)
C(3S)	970(16)	2047(19)	8656(16)	398(20)

Experimental

The ^1H NMR spectra were recorded on a Bruker WM-400 instrument. $CDCl_3$ or C_6D_6 was used as the solvent. The mass spectra were measured on a Hitachi M-80A mass spectrometer (EI, 70 eV). The reaction mixtures were analyzed by TLC on Silufol UV-254 plates. The solid-phase reactions were carried out in a extruder described previously.[2]

Table 3. Coordinates ($\times10^3$) and isotropic thermal parameters ($U\times10^2$/Å^2) of hydrogen atoms of hydroxyl groups in the structure of **6**

Atom	*x*	*y*	*z*	*U*
H(10)	298(5)	−97(4)	777(4)	14(3)
H(10′)	280(3)	−533(3)	282(3)	7(2)

Synthesis of 2-dialkylaminomethyl-4,6-di-*tert*-butylphenols 2a—c (general procedure). A solution of the corresponding amine (190 mmol) in Bu^{n}OH (8 mL) was added to a mixture of a 37% formaldehyde solution (4.5 mL) and Bu^{n}OH (12 mL) at 0 °C. The temperature of the mixture was slowly increased to 20 °C. A solution of 2,4-di-*tert*-butylphenol (10 g, 48 mmol) in a minimum amount of Bu^{n}OH was added to the reaction mixture. The mixture was stirred at 20 °C for 1 h and then stirred for 4 h with heating on a water bath. The reaction mixture was cooled, and H_2O (300 mL) was added. Then the mixture was treated with concentrated HCl until the solution became acidic. The aqueous solution was twice washed with ether to remove unconsumed phenol. The aqueous extracts were alkalified with a 2*N* NaOH solution under ether. The etheral extracts were dried, and the ether was distilled off. Compounds **2a—c** were isolated from the residue.

Compound **2**, m.p. 62—63 °C (from CH_3OH). Found (%): C, 78.01; H, 11.16. $C_{17}H_{29}NO$. Calculated (%): C, 77.60; H, 11.0.

Compound **2b**, m.p. 111—112 °C (from hexane). Found (%): C, 74.89; H, 10.15. $C_{19}H_{31}NO_2$. Calculated (%): C, 74.71; H, 10.24.

Compound **2c**, m.p. 82—84 °C (from hexane). Found (%): C, 80.89; H, 11.0. $C_{27}H_{45}NO$. Calculated (%): C, 81.14; H, 11.35.

Oxidation of 4,6-di-*tert*-butyl-2-dimethylaminomethylphenol (2a). ***A.*** $Mn(OAc)_3$. A mixture of compound **2** (2.63 g, 10 mmol) and $Mn(OAc)_3\cdot2H_2O$ (7 g, 25 mmol) in AcOH (50 mL) was stirred for 2 h, treated with H_2O and Et_2O, and evaporated. Aldehyde **1**, m.p. 62—63 °C (from Me(OH)),[1] and 3,5-di-*tert*-butyl-1-(2-dimethylaminomethyl-4,6-di-*tert*-butylphenoxy)-2-(2-hydroxy-3,5-di-*tert*-butylphenoxy)benzene (**6**), m.p. 138—139 °C (from acetone), were isolated in yields of 0.7 g (31%) and 1.5 g (69%), respectively. Found (%): C, 79.98; H, 9.91. $C_{45}H_{69}NO_3$. Calculated (%): C, 80.42; H, 10.34. Mass spectrum, *m/z*: 672 $[M]^+$. ^{1}H NMR ($CDCl_3$), δ: 0.85, 1.12, 1.19, 1.29, 1.32, 1.51 (s, 9 H, CMe_3); 2.09, 2.15 (s, 3 H, Me); 3.26 (s, 2 H, CH_2); 6.14, 6.61, 6.82, 6.89, 6.97, 7.21 (d, 2 H, Ph).

The same amounts of compound **2a** and $Mn(OAc)_3$ were passed through an extruder. Workup of the reaction mixture according to the procedure described above gave aldehyde **1** and compound **6** in yields of 0.9 g (40%) and 1.2 g (60%), respectively.

B. $Mn(OAc)_3$—$Mn(OAc)_2$. A mixture of compound **2a** (0.13 g, 0.5 mmol), $Mn(OAc)_3\cdot2H_2O$ (0.2 g, 0.75 mmol), and $Mn(OAc)_2\cdot4H_2O$ (0.47 g, 2.5 mmol) was stirred under the conditions of experiment *A*. Aldehyde **1** and compound **7** (m.p. 113—114 °C, from hexane)[3] were isolated in yields of 0.1 g (86%) and 0.02 g (14%), respectively.

Table 4. Bond lengths (*d*/Å) in the structure of **6**

Bond	*d*/Å	Bond	*d*/Å	Bond	*d*/Å	Bond	*d*/Å
Molecule **1**				Molecule **2**			
O(1)—C(2)	1.389(7)	C(19)—C(20)	1.381(9)	O(1′)—C(2′)	1.371(7)	C(17′)—C(42′)	1.517(9)
O(8)—C(9)	1.378(7)	C(19)—C(46)	1.540(1)	O(8′)—C(9′)	1.399(7)	C(18′)—C(19′)	1.396(9)
O(8)—C(7)	1.395(7)	C(20)—C(21)	1.387(9)	O(8′)—C(7′)	1.410(7)	C(19′)—C(20′)	1.391(9)
O(15)—C(14)	1.379(7)	C(21)—C(22)	1.498(9)	O(15′)—C(14′)	1.382(7)	C(19′)—C(46′)	1.548(9)
O(15)—C(16)	1.409(7)	C(26)—C(27)	1.510(1)	O(15′)—C(16′)	1.405(7)	C(20′)—C(21′)	1.379(9)
N(23)—C(22)	1.456(8)	C(26)—C(28)	1.530(1)	N(23′)—C(22′)	1.473(8)	C(21′)—C(22′)	1.503(9)
N(23)—C(24)	1.461(9)	C(26)—C(29)	1.530(1)	N(23′)—C(24′)	1.466(9)	C(26′)—C(27′)	1.514(9)
N(23)—C(25)	1.466(9)	C(30)—C(31)	1.580(1)	N(23′)—C(25′)	1.458(8)	C(26′)—C(28′)	1.542(9)
C(2)—C(3)	1.379(8)	C(30)—C(32)	1.490(2)	C(2′)—C(3′)	1.389(8)	C(26′)—C(29′)	1.544(9)
C(2)—C(7)	1.387(8)	C(30)—C(33)	1.470(2)	C(2′)—C(7′)	1.392(8)	C(30′)—C(31′)	1.570(2)
C(3)—C(4)	1.393(9)	C(30)—C(31A)	1.590(2)	C(3′)—C(4′)	1.392(9)	C(30′)—C(32′)	1.390(2)
C(3)—C(26)	1.540(1)	C(30)—C(32A)	1.640(2)	C(3′)—C(26′)	1.541(9)	C(30′)—C(33′)	1.660(2)
C(4)—C(5)	1.381(9)	C(30)—C(33A)	1.530(3)	C(4′)—C(5′)	1.395(8)	C(30′)—C(31B)	1.670(2)
C(5)—C(6)	1.366(8)	C(34)—C(35)	1.500(1)	C(5′)—C(6′)	1.375(8)	C(30′)—C(32B)	1.510(2)
C(5)—C(30)	1.540(1)	C(34)—C(36)	1.500(1)	C(5′)—C(30′)	1.540(1)	C(30′)—C(33B)	1.380(2)
C(6)—C(7)	1.380(8)	C(34)—C(37)	1.490(1)	C(6′)—C(7′)	1.364(8)	C(34′)—C(35′)	1.540(1)
C(9)—C(10)	1.381(8)	C(38)—C(39)	1.580(2)	C(9′)—C(10′)	1.398(8)	C(34′)—C(36′)	1.520(1)
C(9)—C(14)	1.388(9)	C(38)—C(40)	1.470(1)	C(9′)—C(14′)	1.379(9)	C(34′)—C(37′)	1.545(9)
C(10)—C(11)	1.405(9)	C(38)—C(41)	1.490(1)	C(10′)—C(11′)	1.393(9)	C(38′)—C(39′)	1.500(1)
C(10)—C(34)	1.540(1)	C(38)—C(39A)	1.590(2)	C(10′)—C(34′)	1.526(9)	C(38′)—C(40′)	1.460(1)
C(11)—C(12)	1.364(9)	C(38)—C(40A)	1.670(3)	C(11′)—C(12′)	1.371(9)	C(38′)—C(41′)	1.490(1)
C(12)—C(13)	1.385(9)	C(38)—C(41A)	1.460(3)	C(12′)—C(13′)	1.384(8)	C(42′)—C(43′)	1.537(9)
C(12)—C(38)	1.540(1)	C(42)—C(43)	1.520(1)	C(12′)—C(38′)	1.513(9)	C(42′)—C(44′)	1.542(9)
C(13)—C(14)	1.385(9)	C(42)—C(44)	1.520(1)	C(13′)—C(14′)	1.389(8)	C(42′)—C(45′)	1.539(9)
C(16)—C(17)	1.390(9)	C(42)—C(45)	1.550(1)	C(16′)—C(17′)	1.395(9)	C(46′)—C(47′)	1.530(1)
C(16)—C(21)	1.402(9)	C(46)—C(47)	1.500(1)	C(16′)—C(21′)	1.381(9)	C(46′)—C(48′)	1.520(1)
C(17)—C(18)	1.389(9)	C(46)—C(48)	1.500(1)	C(17′)—C(18′)	1.380(9)	C(46′)—C(49′)	1.530(1)
C(17)—C(42)	1.542(9)	C(46)—C(49)	1.520(1)				
C(18)—C(19)	1.371(9)						

Table 5. Bond angles (ω/deg) in the structure of **6**

Angle	ω/deg
Molecule **1**	
C(9)—O(8)—C(7)	118.9(5)
C(14)—O(15)—C(16)	117.2(5)
C(22)—N(23)—C(24)	109.6(6)
C(22)—N(23)—C(25)	112.1(6)
C(24)—N(23)—C(25)	109.7(7)
C(3)—C(2)—C(7)	120.5(6)
C(3)—C(2)—O(1)	121.0(6)
C(7)—C(2)—O(1)	118.5(6)
C(2)—C(3)—C(4)	116.9(6)
C(2)—C(3)—C(26)	122.3(7)
C(4)—C(3)—C(26)	120.8(7)
C(5)—C(4)—C(3)	123.6(6)
C(6)—C(5)—C(4)	117.5(6)
C(6)—C(5)—C(30)	121.5(7)
C(4)—C(5)—C(30)	120.9(7)
C(5)—C(6)—C(7)	120.9(6)
C(6)—C(7)—C(2)	120.4(6)
C(6)—C(7)—O(8)	124.2(6)
C(2)—C(7)—O(8)	115.2(6)
O(8)—C(9)—C(10)	122.3(7)
O(8)—C(9)—C(14)	116.8(6)
C(10)—C(9)—C(14)	120.2(7)
C(9)—C(10)—C(11)	116.1(7)
C(9)—C(10)—C(34)	122.4(7)
C(11)—C(10)—C(34)	121.4(6)
C(12)—C(11)—C(10)	124.8(7)
C(11)—C(12)—C(13)	117.8(7)
C(11)—C(12)—C(38)	122.7(8)
C(13)—C(12)—C(38)	119.5(8)
C(12)—C(13)—C(14)	119.2(7)
O(15)—C(14)—C(13)	121.7(7)
O(15)—C(14)—C(9)	116.5(6)
C(13)—C(14)—C(9)	121.8(7)
C(17)—C(16)—C(21)	123.1(7)
C(17)—C(16)—O(15)	119.3(7)
C(21)—C(16)—O(15)	117.5(7)
C(18)—C(17)—C(16)	115.8(7)
C(18)—C(17)—C(42)	121.7(7)
C(16)—C(17)—C(42)	122.5(7)
C(19)—C(18)—C(17)	124.3(7)
C(18)—C(19)—C(20)	117.0(7)
C(18)—C(19)—C(46)	124.4(8)
C(20)—C(19)—C(46)	118.6(8)
C(19)—C(20)—C(21)	123.2(7)
C(20)—C(21)—C(16)	116.5(7)
C(20)—C(21)—C(22)	121.6(7)
C(16)—C(21)—C(22)	121.9(7)
N(23)—C(22)—C(21)	114.4(6)
C(27)—C(26)—C(28)	109.2(7)
C(27)—C(26)—C(29)	108.7(8)
C(28)—C(26)—C(29)	107.7(8)
C(27)—C(26)—C(3)	110.4(7)
C(28)—C(26)—C(3)	108.4(7)
C(29)—C(26)—C(3)	112.3(7)
C(33)—C(30)—C(32)	113.0(1)
C(33)—C(30)—C(5)	108.1(9)
C(32)—C(30)—C(5)	112.5(8)
C(33A)—C(30)—C(5)	115.0(1)
C(33)—C(30)—C(31)	107.0(1)
C(32)—C(30)—C(31)	107.0(1)
C(5)—C(30)—C(31)	109.6(7)
C(33A)—C(30)—C(31A)	121.0(2)
C(5)—C(30)—C(31A)	109.0(1)
C(33A)—C(30)—C(32A)	98.0(2)
C(5)—C(30)—C(32A)	108.0(1)
C(31A)—C(30)—C(32A)	108.0(1)
C(37)—C(34)—C(35)	104.1(9)
C(37)—C(34)—C(36)	106.6(9)
C(35)—C(34)—C(36)	108.9(9)
C(37)—C(34)—C(10)	111.9(7)
C(35)—C(34)—C(10)	109.4(7)
C(36)—C(34)—C(10)	110.9(7)
C(40)—C(38)—C(41)	114.0(1)
C(41A)—C(38)—C(12)	116.0(2)
C(40)—C(38)—C(12)	108.4(8)
C(41)—C(38)—C(12)	109.6(7)
C(40)—C(38)—C(39)	110.0(1)
C(41)—C(38)—C(39)	105.8(9)
C(12)—C(38)—C(39)	108.8(9)
C(41A)—C(38)—C(39A)	109.0(2)
C(12)—C(38)—C(39A)	109.0(1)
C(41A)—C(38)—C(40A)	114.0(2)
C(12)—C(38)—C(40A)	112.0(1)
C(39A)—C(38)—C(40A)	95.0(2)
C(44)—C(42)—C(43)	107.6(7)
C(44)—C(42)—C(17)	110.4(6)
C(43)—C(42)—C(17)	111.6(6)
C(44)—C(42)—C(45)	109.9(7)
C(43)—C(42)—C(45)	107.0(7)
C(17)—C(42)—C(45)	110.2(6)
C(47)—C(46)—C(48)	108.7(9)
C(47)—C(46)—C(49)	109.0(9)
C(48)—C(46)—C(49)	109.0(1)
C(47)—C(46)—C(19)	111.1(8)
C(48)—C(46)—C(19)	110.3(8)
C(49)—C(46)—C(19)	108.8(8)
Molecule **2**	
C(9′)—O(8′)—C(7′)	117.4(5)
C(14′)—O(15′)—C(16′)	117.5(5)
C(25′)—N(23′)—C(24′)	111.0(7)
C(25′)—N(23′)—C(22′)	109.9(6)
C(24′)—N(23′)—C(22′)	110.6(6)
O(1′)—C(2′)—C(3′)	120.5(7)
O(1′)—C(2′)—C(7′)	120.1(6)
C(3′)—C(2′)—C(7′)	119.4(7)
C(2′)—C(3′)—C(4′)	117.5(6)
C(2′)—C(3′)—C(26′)	120.9(6)
C(4′)—C(3′)—C(26′)	121.6(6)
C(3′)—C(4′)—C(5′)	122.7(6)
C(6′)—C(5′)—C(4′)	118.2(6)
C(6′)—C(5′)—C(30′)	121.2(7)
C(4′)—C(5′)—C(30′)	120.4(6)
C(7′)—C(6′)—C(5′)	119.8(6)
C(6′)—C(7′)—C(2′)	122.1(6)
C(6′)—C(7′)—O(8′)	122.9(6)
C(2′)—C(7′)—O(8′)	114.8(6)
C(14′)—C(9′)—C(10′)	121.4(7)
C(14′)—C(9′)—O(8′)	117.2(6)
C(10′)—C(9′)—O(8′)	120.5(7)
C(11′)—C(10′)—C(9′)	115.7(7)
C(11′)—C(10′)—C(34′)	121.9(7)
C(9′)—C(10′)—C(34′)	122.4(7)
C(12′)—C(11′)—C(10′)	124.6(6)
C(11′)—C(12′)—C(13′)	117.8(6)
C(11′)—C(12′)—C(38′)	122.2(7)
C(13′)—C(12′)—C(38′)	120.0(7)
C(12′)—C(13′)—C(14′)	120.2(7)
C(9′)—C(14′)—O(15′)	116.8(6)
C(9′)—C(14′)—C(13′)	120.3(7)
O(15′)—C(14′)—C(13′)	122.9(7)
C(21′)—C(16′)—C(17′)	123.6(7)
C(21′)—C(16′)—O(15′)	118.1(6)
C(17′)—C(16′)—O(15′)	118.1(7)
C(18′)—C(17′)—C(16′)	115.3(7)
C(18′)—C(17′)—C(42′)	121.5(7)
C(16′)—C(17′)—C(42′)	123.0(7)
C(17′)—C(18′)—C(19′)	124.3(7)
C(20′)—C(19′)—C(18′)	116.6(6)
C(20′)—C(19′)—C(46′)	120.9(7)
C(18′)—C(19′)—C(46′)	122.4(7)
C(21′)—C(20′)—C(19′)	122.2(7)
C(20′)—C(21′)—C(16′)	117.8(7)
C(20′)—C(21′)—C(22′)	120.5(7)
C(16′)—C(21′)—C(22′)	121.7(7)
N(23′)—C(22′)—C(21′)	114.3(6)
C(27′)—C(26′)—C(3′)	111.5(6)
C(27′)—C(26′)—C(28′)	107.4(6)
C(3′)—C(26′)—C(28′)	111.3(6)
C(27′)—C(26′)—C(29′)	110.4(6)
C(3′)—C(26′)—C(29′)	109.5(6)
C(28′)—C(26′)—C(29′)	106.6(6)
C(33B)—C(30′)—C(32B)	113.0(1)
C(33B)—C(30′)—C(5′)	114.0(1)
C(32′)—C(30′)—C(5′)	118.0(1)
C(32B)—C(30′)—C(5′)	111.4(9)
C(32′)—C(30′)—C(31′)	117.0(1)
C(5′)—C(30′)—C(31′)	108.9(8)
C(32′)—C(30′)—C(33′)	105.0(1)
C(5′)—C(30′)—C(33′)	105.8(9)
C(31′)—C(30′)—C(33′)	101.0(1)
C(33B)—C(30′)—C(31B)	109.0(1)
C(32B)—C(30′)—C(31B)	101.2(9)
C(5′)—C(30′)—C(31B)	108.1(8)
C(36′)—C(34′)—C(10′)	110.3(6)
C(36′)—C(34′)—C(35′)	109.8(7)
C(10′)—C(34′)—C(35′)	110.6(6)
C(36′)—C(34′)—C(37′)	107.1(7)
C(10′)—C(34′)—C(37′)	111.8(6)
C(35′)—C(34′)—C(37′)	107.2(6)
C(40′)—C(38′)—C(41′)	109.0(1)
C(40′)—C(38′)—C(39′)	105.9(9)
C(41′)—C(38′)—C(39′)	107.0(1)
C(40′)—C(38′)—C(12′)	110.0(7)
C(41′)—C(38′)—C(12′)	110.7(7)
C(39′)—C(38′)—C(12′)	113.9(8)
C(17′)—C(42′)—C(43′)	110.5(6)
C(17′)—C(42′)—C(45′)	112.2(6)
C(43′)—C(42′)—C(45′)	106.1(6)
C(17′)—C(42′)—C(44′)	111.1(6)
C(43′)—C(42′)—C(44′)	110.3(6)
C(45′)—C(42′)—C(44′)	106.5(6)
C(48′)—C(46′)—C(49′)	110.9(7)
C(48′)—C(46′)—C(47′)	108.9(7)
C(49′)—C(46′)—C(47′)	108.4(7)
C(48′)—C(46′)—C(19′)	111.6(7)
C(49′)—C(46′)—C(19′)	108.2(6)
C(47′)—C(46′)—C(19′)	108.8(6)

Table 6. Coordinates (×10^4) and equivalent isotropic thermal parameters (×10^3) of nonhydrogen atoms in the structure of **5**

Atom	x	y	z	U_{eq}	Atom	x	y	z	U_{eq}
		Molecule **1**					Molecule **1′**		
O(5)	4637(5)	−2029(9)	5591(3)	47(2)	O(5′)	7834(5)	−2946(8)	6919(3)	44(2)
O(8)	2651(6)	−2535(10)	6029(3)	64(3)	O(8′)	9806(7)	−2438(10)	6470(3)	68(3)
N(11)	3473(10)	−6(8)	5607(5)	32(4)	N(11′)	9049(11)	−4965(9)	6887(5)	47(4)
C(1)	5289(9)	239(12)	4632(4)	35(3)	C(1′)	7168(11)	−5361(15)	7844(5)	49(4)
C(2)	5995(9)	−597(13)	4413(4)	38(3)	C(2′)	6454(9)	−4533(13)	8084(4)	37(3)
C(3)	6205(8)	−1961(12)	4591(4)	40(3)	C(3′)	6245(8)	−3139(13)	7914(4)	39(3)
C(4)	5757(8)	−2483(12)	4978(3)	37(3)	C(4′)	6683(8)	−2555(12)	7528(3)	34(3)
C(4A)	5065(8)	−1553(11)	5198(3)	36(3)	C(4A′)	7388(8)	−3497(11)	7307(4)	35(3)
C(6)	4114(9)	−930(12)	5853(4)	44(3)	C(6′)	8352(9)	−4026(12)	6647(4)	43(3)
C(7)	3521(10)	−1743(13)	6203(4)	62(4)	C(7′)	8928(10)	−3153(12)	6299(4)	53(3)
C(9)	2007(10)	−1531(14)	5798(4)	65(4)	C(9′)	10490(11)	−3402(15)	6705(4)	71(4)
C(10)	2559(10)	−762(15)	5426(4)	54(4)	C(10′)	9916(9)	−4149(14)	7082(4)	47(3)
C(12)	4064(9)	779(13)	5273(4)	51(3)	C(12′)	8442(9)	−5789(13)	7211(4)	49(3)
C(12A)	4808(11)	−183(12)	5027(5)	32(4)	C(12B)	7642(12)	−4856(12)	7461(5)	39(4)
C(13)	6604(14)	−117(13)	3999(7)	45(5)	C(13′)	5941(11)	−5066(13)	8507(7)	43(5)
C(14)	7812(13)	12(14)	4087(8)	64(6)	C(14′)	4805(11)	−5017(12)	8438(7)	43(5)
C(15)	6403(12)	−1224(16)	3620(5)	72(5)	C(15′)	6210(12)	−6623(15)	8634(6)	81(5)
C(16)	6140(11)	1340(15)	3820(5)	71(5)	C(16′)	6183(12)	−3987(20)	8884(5)	80(5)
C(17)	6040(9)	−4013(13)	5163(4)	42(3)	C(17′)	6398(9)	−1041(13)	7358(4)	44(3)
C(18)	6563(11)	−3842(16)	5621(4)	67(4)	C(18′)	5611(14)	−276(15)	7674(7)	83(7)
C(19)	5046(16)	−4928(12)	5200(7)	58(6)	C(19′)	7371(16)	−68(14)	7337(9)	72(6)
C(20)	6806(15)	−4837(13)	4874(6)	69(6)	C(20′)	5895(10)	−1144(16)	6906(5)	69(4)

Table 7. Bond angles (ω) in the structure of **5**

Angle	ω/deg
Molecule **1**	
C(4A)—O(5)—C(6)	115.8(8)
C(7)—O(8)—C(9)	108.0(1)
C(6)—N(11)—C(10)	113.0(1)
C(6)—N(11)—C(12)	111.0(1)
C(12)—N(11)—C(10)	113.0(1)
C(2)—C(1)—C(12A)	124.0(1)
C(1)—C(2)—C(3)	117.0(1)
C(1)—C(2)—C(13)	125.0(1)
C(3)—C(2)—C(13)	118.0(1)
C(2)—C(3)—C(4)	124.0(1)
C(3)—C(4)—C(4A)	117.0(1)
C(3)—C(4)—C(17)	121.0(1)
C(4A)—C(4)—C(17)	122.0(1)
O(5)—C(4A)—C(12A)	121.0(1)
O(5)—C(4A)—C(4)	118.0(9)
C(12A)—C(4A)—C(4)	121.0(1)
N(11)—C(6)—O(5)	114.0(1)
N(11)—C(6)—C(7)	112.0(1)
O(5)—C(6)—C(7)	105.9(9)
O(8)—C(7)—C(6)	113.0(1)
O(8)—C(9)—C(10)	113.0(1)
N(11)—C(10)—C(9)	109.0(1)
N(11)—C(12)—C(12A)	113.0(1)
C(4A)—C(12A)—C(1)	118.0(1)
C(4A)—C(12A)—C(12)	120.0(1)
C(1)—C(12A)—C(12)	123.0(1)
C(2)—C(13)—C(14)	109.0(1)
C(2)—C(13)—C(15)	112.0(2)
C(2)—C(13)—C(16)	110.0(1)
C(15)—C(13)—C(14)	110.0(2)
C(15)—C(13)—C(16)	112.0(1)
C(16)—C(13)—C(14)	104.0(2)
C(18)—C(17)—C(4)	109.0(1)
C(19)—C(17)—C(4)	109.0(1)
C(20)—C(17)—C(4)	113.0(1)
C(19)—C(17)—C(18)	111.0(1)
C(20)—C(17)—C(18)	107.0(1)
C(20)—C(17)—C(19)	108.0(1)
Molecule **1′**	
C(4A′)—O(5′)—C(6′)	114.6(8)
C(7′)—O(8′)—C(9′)	113.0(1)
C(6′)—N(11′)—C(10′)	111.6(9)
C(6′)—N(11′)—C(12′)	109.0(1)
C(12′)—N(11′)—C(10′)	114.0(1)
C(2′)—C(1′)—C(12A′)	123.0(1)
C(1′)—C(2′)—C(3′)	116.0(1)
C(1′)—C(2′)—C(13′)	123.0(1)
C(3′)—C(2′)—C(13′)	121.0(1)
C(2′)—C(3′)—C(4′)	125.0(1)
C(3′)—C(4′)—C(4A′)	115.0(1)
C(3′)—C(4′)—C(17′)	122.0(1)
C(4A′)—C(4′)—C(17′)	123.2(9)
C(5′)—C(4A′)—O(12′A)	121.0(1)
C(5′)—C(4A′)—C(4′)	115.9(9)
O(12A′)—C(4A′)—C(4′)	123.0(1)
N(11′)—C(6′)—O(5′)	114.0(1)
N(11′)—C(6′)—C(7′)	111.0(1)
O(5′)—C(6′)—C(7′)	104.9(8)
O(8′)—C(7′)—C(6′)	112.0(1)
O(8′)—C(9′)—C(10′)	111.0(1)
N(11′)—C(10′)—C(9′)	107.0(1)
N(11′)—C(12′)—C(12A′)	113.0(1)
C(4A′)—C(12A′)—C(1′)	119.0(1)
C(4A′)—C(12A′)—C(12′)	120.0(1)
C(1′)—C(12A′)—C(12′)	121.0(1)
C(2′)—C(13′)—C(14′)	108.0(1)
C(2′)—C(13′)—C(15′)	115.0(1)
C(2′)—C(13′)—C(16′)	109.0(1)
C(15′)—C(13′)—C(14′)	107.0(1)
C(15′)—C(13′)—C(16′)	112.0(2)
C(16′)—C(13′)—C(14′)	106.0(1)
C(18′)—C(17′)—C(4′)	111.0(1)
C(19′)—C(17′)—C(4′)	110.0(1)
C(20′)—C(17′)—C(4′)	110.0(1)
C(19′)—C(17′)—C(18′)	107.0(1)
C(20′)—C(17′)—C(18′)	108.0(1)
C(20′)—C(17′)—C(19′)	110.0(1)

C. PbO_2. A mixture of compound **2a** (0.4 g, 1.5 mmol) and PbO_2 (1.8 g, 7.5 mmol) in C_6H_6 (30 mL) was stirred for 3 h. Then the reaction mixture was poured into water and extracted with ether. The solvent was evaporated. The resulting oil was dissolved in MeOH, and aldehyde **1** was isolated in a yield of 70 mg (20%). The remaining oil was distilled *in vacuo.* 6,8-Di-*tert*-butyl-3-methyl-2*H*-3,4-dihydrobenzo[e]-1,3-oxazine (**4**) was obtained in a yield of 0.32 g (80%), b.p. 114—

Table 8. Bond lengths (*d*) in the structure of 5

Bond	*d*/Å	Bond	*d*/Å
Molecule **1**		Molecule **1′**	
O(5)—C(4A)	1.38(1)	O(5′)—C(4A′)	1.40(1)
O(5)—C(6)	1.45(1)	O(5′)—C(6′)	1.45(1)
O(8)—C(7)	1.43(1)	O(8′)—C(7′)	1.40(1)
O(8)—C(9)	1.42(1)	O(8′)—C(9′)	1.43(1)
N(11)—C(6)	1.39(2)	N(11′)—C(6′)	1.44(2)
N(11)—C(12)	1.45(2)	N(11′)—C(12′)	1.46(2)
N(11)—C(10)	1.47(2)	N(11′)—C(10′)	1.46(2)
C(1)—C(2)	1.36(2)	C(1′)—C(12B)	1.39(2)
C(1)—C(12A)	1.40(2)	C(1′)—C(2′)	1.39(2)
C(2)—C(3)	1.39(2)	C(2′)—C(3′)	1.40(2)
C(2)—C(13)	1.54(2)	C(2′)—C(13′)	1.52(2)
C(3)—C(4)	1.39(1)	C(3′)—C(4′)	1.40(1)
C(4)—C(4A)	1.40(1)	C(4′)—C(4A′)	1.42(1)
C(4)—C(17)	1.55(2)	C(4′)—C(17′)	1.52(2)
C(4A)—C(12A)	1.40(1)	C(4A′)—C(12A′)	1.37(1)
C(6)—C(7)	1.50(2)	C(6′)—C(7′)	1.51(2)
C(9)—C(10)	1.50(2)	C(9′)—C(10′)	1.52(2)
C(12)—C(12A)	1.50(2)	C(12′)—C(12A′)	1.53(2)
C(13)—C(14)	1.57(2)	C(13′)—C(14′)	1.47(2)
C(13)—C(15)	1.55(2)	C(13′)—C(15′)	1.52(2)
C(13)—C(16)	1.56(2)	C(13′)—C(16′)	1.54(2)
C(17)—C(18)	1.54(2)	C(17′)—C(18′)	1.55(2)
C(17)—C(19)	1.53(2)	C(17′)—C(19′)	1.53(2)
C(17)—C(20)	1.51(2)	C(17′)—C(20′)	1.51(2)

116 °C (1 Torr). Found (%): C, 78.0; H, 10.34. $C_{17}H_{27}NO$. Calculated (%): C, 78.1; H, 10.34. ^{1}H NMR (C_6D_6), δ: 1.31, 1.56 (s, 9 H, CMe$_3$); 2.34 (s, 3 H, Me); 3.71, 4.51 (s, 2 H, CH$_2$); 6.78, 7.36 (d, 2 H, Ph). The structure of 4 was also confirmed by its reduction by a solution of NaBH$_4$ in Pr^{i}OH, which yielded initial compound **2a**. A mixture of phenol **2a** (2 g) and PbO$_2$ (9 g) was passed through an extruder. Then the reaction mixture was treated with ether, and the solvent was evaporated. Aldehyde **1** and compound **4** were isolated in yields of 0.7 g (40%) and 1.2 g (60%), respectively.

Oxidation of 4,6-di-*tert*-butyl-2-morpholinomethylphenol (2b). A mixture of phenol **2b** (0.6 g, 2 mmol) and PbO$_2$ (2.4 g, 10 mmol) in C_6H_6 (40 mL) was stirred for 3 h. Then the reaction mixture was poured into water and extracted with ether. The solvent was evaporated. Aldehyde **1**, 1,1′-dihydroxy-2,2′,4,4′-tetra-*tert*-butyldiphenyl (**3**), m.p. 185—186 °C (from MeOH),[4] and 8,9-(2,4-di-*tert*-butyl)benzo-1-aza-4,7-dioxabicyclo[4.4.0]decane (**5**), m.p. 140—141 °C (from hexane), were isolated from the resulting oil in yields of 0.1 g (21%), 0.08 g (9%), and 0.4 g (70%), respectively. Compound **5**. Found (%): C, 75.2; H, 9.63. $C_{19}H_{29}NO_2$. Calculated (%): C, 74.98; H, 9.53. ^{1}H NMR (CDCl$_3$), δ: 1.28, 1.39 (s, 9 H, CMe$_3$); 2.48 (m, 2 H, CH$_2$N, ^2J = 11.6 Hz); 3.11 (m, 2 H, CH$_2$N, ^3J = 3.1 and 8.5 Hz); 3.65 (d, 2 H, <u>CH</u>$_2$Ph); 4.25 (d, 2 H, <u>CH</u>$_2$Ph, ^2J = 15.9 Hz); 3.88 (m, 2 H, CH$_2$O); 4.65 (t, 1 H, HCO, ^3J = 2.1 and 2.8 Hz); 6.82 (d, 1 H, Ph, ^4J = 2.1 Hz); 7.17 (d, 1 H, Ph, ^4J = 2.1 Hz). Mass spectrum, *m/z*: 303 [M]$^+$.

A mixture of phenol **2b** (3 g) and PbO$_2$ (12 g) was passed through an extruder and treated with ether. After evaporation of the solvent, aldehyde **1** (0.7 g, 30%), compound **3** (0.2 g, 5%), and compound **5** (1.9 g, 65%) were isolated.

Oxidation of 4,6-di-*tert*-butyl-2-dicyclohexylaminomethylphenol (2c). A mixture of phenol **2** (0.2 g, 0.5 mmol) and Mn(OAc)$_3$ · 2H$_2$O (0.34 g, 1.3 mmol) in AcOH (30 mL) was stirred for 2 h. Then the reaction mixture was poured into H$_2$O, extracted with ether, and dried. After removal of the solvent, mixture of compounds **3** (in a yield of 0.1 g (95%)) and **1** (<5%, identified by TLC) was isolated.

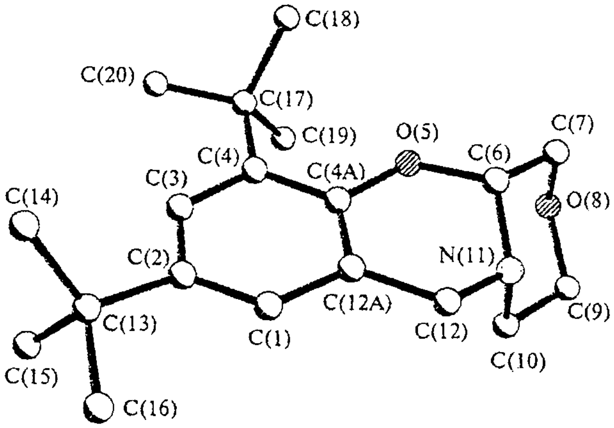


Fig. 3. Structure of compound 5.

X-ray structural analysis. The structures of compounds **5** and **6** were established with the use of the SHELX-93 program package. Crystals of **6** ($C_{45}H_{69}NO_3 \cdot 0.5\ C_3H_6O$, *M* = 701.05) are monoclinic, space group $P2_1/n$, at 20 °C: *a* = 20.075 (6), *b* = 20.282 (7), *c* = 23.702 (9) Å, β = 104.31 (3)°, *V* = 9351 (6) Å^3, *z* = 8, d_{calc} = 0.996 g/cm^3. The unit cell parameters and intensities of 10171 reflections were measured on an automated four-circle Siemens P3/PC diffractometer (293 K, λMo-Kα radiation, graphite monochromator, θ/2θ scanning technique, θ_{max} = 22°). The structure was solved by the direct method and refined by the full-matrix least-squares method with anisotropic thermal parameters for nonhydrogen atoms except for the C(31), C(32), C(33), C(39), C(40), C(41) and C(31′), C(32′), and C(33′) atoms of three *tert*-butyl groups, which were disordered at two sites (with equal occupancies) and refined isotropically. The positions of the H atoms of the hydroxyl groups were located from the difference Fourier synthesis and refined isotropically. The positions of the other H atoms were calculated geometrically (except for the H atoms of the solvate acetone molecule whose position cannot be adequately calculated because of the high thermal vibrations of this molecule). The above-mentioned H atoms were refinement isotropically with fixed positional (the riding model) and thermal (for the methyl groups, the values of U_{iso} of the H atoms were equal to 1.5 U_{iso} of C atoms, and for the other groups, the values of U_{iso} of the H atoms were equal to 1.2 U_{iso} of C atoms) parameters. The final values of the *R* factors were as follows: R_1 = 0.900 based on 7785 independent reflections with $I > 2\sigma(I)$ and wR_2 = 0.311 using a total of 9777 independent reflections. The atomic coordinates and thermal parameters are given in Tables 2 and 3. The bond lengths and bond angles are given in Tables 4 and 5, respectively.

Crystals of compound **5** (Fig. 3) ($C_{19}H_{29}NO_2$, *M* = 303.43) are orthorhombic, space group $Pca2_1$, at 20 °C: *a* = 12.801 (2), *b* = 9.160(2), *c* = 30.197(5) Å, *V* = 3541(1) Å^3, *z* = 8, d_{calc} = 1.138 g/cm^3. The unit cell parameters and intensities of 2331 reflections were measured on an automated four-circle Syntex R2$_1$ diffractometer (20 °C, λMo-Kα radiation, β filter, θ/2θ scanning technique, θ_{max} = 23 °C). The structure was solved by the direct method and refined by the full-matrix least-squares method with anisotropic thermal parameters for the C atoms of the *tert*-butyl groups. The remaining nonhydrogen atoms were refined isotropically. The hydrogen atoms whose positions were calculated from geometric considerations were refined using the riding model. The final values of the R factors were as follows: $R_1 = 0.072$ based on 2298 independent reflections with $I > 2\sigma(I)$ and $wR_2 = 0.229$ using a total of 2331 independent reflections. The atomic coordinates, bond lengths, bond angles, and isotropic equivalent thermal parameters are given in Tables 6—8.

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