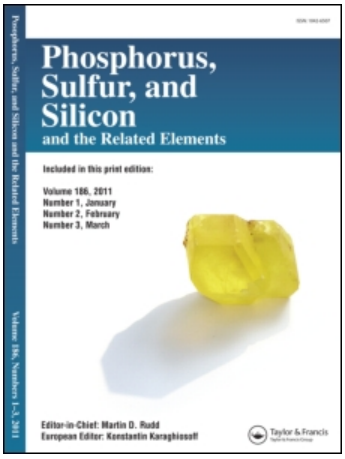

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STABLE QUINONE METHIDES II: ADDITION OF THIOLS TO QUINONE METHIDES, SYNTHESIS OF BISALKYLTHIOSUBSTITUTED QUINONE METHIDES AND TRITHIO-ORTHOBENZOATES

Hansrudolf Meier[a]; Hanspeter Kuenzi[a]; Hermann-fuhrer[b]; Günther Rist[b]
[a] Research Laboratories, Additives Division, Ciba Geigy Limited, Marly, Switzerland [b] Physics Department, Ciba Geigy Limited, CH-4000 Basel, Ulrich Mareis, Central Analytics Department, Ciba Geigy Limited, Marly, Switzerland

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STABLE QUINONE METHIDES II: ADDITION OF THIOLS TO QUINONE METHIDES, SYNTHESIS OF BISALKYLTHIOSUBSTITUTED QUINONE METHIDES AND TRITHIO-ORTHOBENZOATES

HANSRUDOLF MEIER* and HANSPETER KUENZI
Research Laboratories, Additives Division, Ciba Geigy Limited, CH-1723 Marly, Switzerland

and

HERMANN FUHRER and GÜNTHER RIST
Physics Department, Ciba Geigy Limited, CH-4000 Basel, Ulrich Mareis, Central Analytics Department, Ciba Geigy Limited, CH-1723 Marly, Switzerland

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Regioselective oxidation of the *p*-alkylthiomethylphenols **1** with $K_3[Fe(CN)_6]$ to the monosubstituted *p*-quinone methides **2** followed by addition of thiols R^3SH gives rise to the dithioacetals **3**.[1] This reaction sequence can be extended to introduce a third RS substituent by repeating the above mentioned reactions. Spectroscopic data, especially ^{1}H-NMR and ^{13}C-NMR data of the quinone methides **4** and the new trithio-orthoesters **5** are discussed. The same regioselectivity as for the oxidation of **1a**[1] is observed when compounds with two different activated benzylic positions e.g. **3a** and **3b** are oxidized with $K_3[Fe(CN)_6]$. The sequence **1** → **2** → **3** → **4** → **5** constitutes a new approach to trithio-orthoesters.

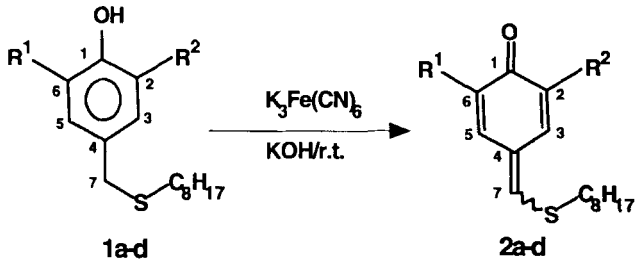
Key words: Synthesis of *p*-quinone methides, synthesis of trithioorthoesters, addition of thiols to *p*-quinone methides.

The regioselective synthesis of the quinone methide **2a** (Scheme I) and 1,6-additions of radicals and nucleophiles to **2a** (a synthetic equivalent of the α-alkylthiobenzyl-cation **Ca**, see Scheme II), as described recently, has opened a new access to *p*-hydroxybenzaldehyde dithioacetals (**3**).[1] Products of this type can be used as antioxidants in polymers.[2]

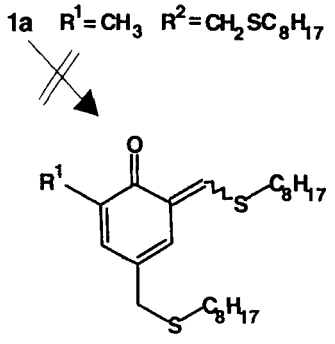
We now report an extension of this synthetic scheme to a sequence including an additional pair of oxidation/addition reactions (Scheme II).

SYNTHESIS OF *p*-QUINONE METHIDES **2a–h** AND *p*-HYDROXYBENZALDEHYDE DITHIOACETALS **3a–h**

Oxidation of the *p*-hydroxybenzylthioethers **1a–d** with $K_3Fe(CN)_6$[1] gives rise to quinone methides **2a–h**, red-orange products in yields of >95% without further purification. Compounds **2a–h** were characterized by IR-, UV-, ^{1}H-NMR- and ^{13}C-NMR-spectroscopy (Tables I and II, and experimental part, cf. Reference 1). Nuclear Overhauser enhancements were used to distinguish between *cis* and *trans* isomers (**2d**). Addition of thiols R^3SH in hexane solution leads to formation of the corre-



1a-d 2a-d [1]



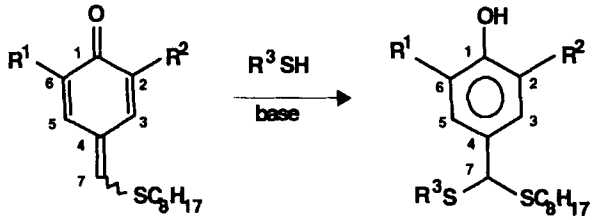
A

SCHEME I

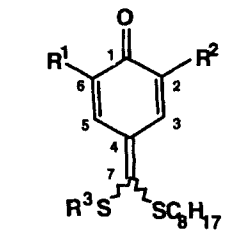
sponding dithioacetals **3a–h** in good yields (66–100%); base catalysis with 10 mol% triethylamine or 250 mol% 1N NaOH (2-phase system) accelerates the addition. Purification of the crude product was carried out by flash chromatography on silica gel. The spectral data of **3a–h** reflect the variation of the substitution pattern (see Tables III, IV, IX, and experimental part[1]). A small part of the NMR data was published in Reference 1; they are included in this paper for the sake of completeness. Tables I–VIII constitute an interesting body of data for sulfur substituted aliphatic carbons. The mass spectra of **3c–h** partly show very weak $M^{+\cdot}$ intensities; in these cases the molecular mass was confirmed by DCI (Desorption Chemical Ionization); the base peak represents the typical loss of the R^3S fragment (see Table IX).

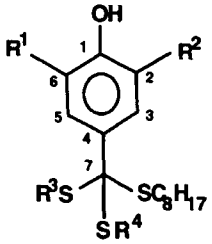
SYNTHESIS OF *p*-QUINONE METHIDES **4a–g**

Oxidation of the dithioacetals **3a–c** and **3e–h** with $K_3Fe(CN)_6$[1] affords doubly substituted quinone methides **4a–g** which—in the same way as their monosubstituted analogs **2**—were not subjected to further purification (yield 90–100%). The same regioselectivity as for **1a** was found for the oxidation of compounds **3a–b** with $K_3Fe(CN)_6$, i.e. selective oxidation at C(7)[1]; ^{1}H-NMR NOE experiments excluded the presence of *o*-quinone methides in concentrations detectable by ^{1}H-NMR (see Tables V, cf. Reference 1). Dyall[3] reported ^{1}H-NMR data of sulfur free analogs of **4a–g**, offering an explanation for the nonequivalence of the ring protons in *p*-quinone methides with two different substituents at C(7). Hindered rotation around the

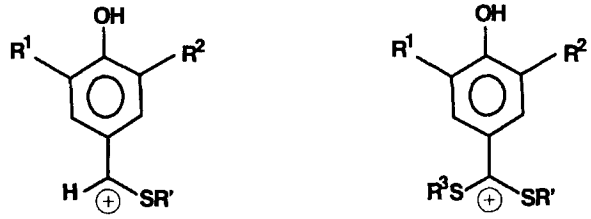


2a-d 3a-h





5a-g 4a-g



R' = alkyl

Ca Cb

	R^1	R^2	R^3	R^4
1a	CH_3	$CH_2SC_8H_{17}$		
1b	CH_3	CH_3		
1c	t-But	t-But		
1d	CH_3	t-But		
2a	CH_3	$CH_2SC_8H_{17}$		
2b	CH_3	CH_3		
2c	t-But	t-But		
2d	CH_3	t-But		
3a	CH_3	$CH_2SC_8H_{17}$	C_8H_{17}	
3b	CH_3	$CH_2SC_8H_{17}$	CH_2COOCH_3	

SCHEME II

	R^1	R^2	R^3	R^4
3c	CH_3	CH_3	C_8H_{17}	
3d	CH_3	CH_3	CH_2COOCH_3	
3e	t-But	t-But	C_8H_{17}	
3f	t-But	t-But	CH_2COOCH_3	
3g	CH_3	t-But	C_8H_{17}	
3h	CH_3	t-But	CH_2COOCH_3	
4a	CH_3	$CH_2SC_8H_{17}$	C_8H_{17}	
4b	CH_3	$CH_2SC_8H_{17}$	CH_2COOCH_3	
4c	CH_3	CH_3	C_8H_{17}	
4d	t-But	t-But	C_8H_{17}	
4e	t-But	t-But	CH_2COOCH_3	
4f	CH_3	t-But	C_8H_{17}	
4g	CH_3	t-But	CH_2COOCH_3	
5a	CH_3	$CH_2SC_8H_{17}$	C_8H_{17}	C_8H_{17}
5b	CH_3	$CH_2SC_8H_{17}$	CH_2COOCH_3	Benzyl
5c	CH_3	CH_3	C_8H_{17}	C_8H_{17}
5d	t-But	t-But	C_8H_{17}	C_8H_{17}
5e	t-But	t-But	CH_2COOCH_3	Benzyl
5f	CH_3	t-But	C_8H_{17}	C_8H_{17}
5g	CH_3	t-But	CH_2COOCH_3	Benzyl

SCHEME II (*Continued*)

TABLE I

^{1}H-NMR chemical shifts [ppm] of compounds **2b–d**[a]

Compound	CH_3-C(2) or CH_2-C(2) or t-Bu-C(2)	H-C(3)	CH-C(4)	H-C(5)	CH_3-C(6) or t-Bu-C(6)
cis-**2a**	3.57 (s)	6.87 (d)	7.17 (s)	7.45 (d)	2.02 (s)
trans-**2a**	3.55 (s)	7.32 (d)	7.20 (s)	7.01 (d)	2.05 (s)
2b	1.95 (s)	7.23 (m)	6.95 (m)	6.75 (m)	1.92 (s)
2c	1.33 (s)	7.27 (d)	7.06 (s)	6.82 (d)	1.30 (s)
cis-**2d**	2.03 (s)	7.27 (d)	7.08 (s)	6.84 (d)	1.31 (s)
trans-**2d**	1.97 (s)	6.80 (d)	7.05 (s)	7.30 (d)	1.28 (s)

[a] Assignments verified by double resonance and or nuclear Overhauser experiments (NOE); $CDCl_3$ soln. at 25°.

TABLE II

^{13}C-NMR chemical shifts [ppm] of compounds **2a, 2b** and **2d**[a]

Comp.	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	CH_3-C(2) CH_2-C(2) t-Bu-C(2)	CH-C(4)	CH_3-C(6) t-But-C(6)
trans-**2a**	185.7 (s)	133.0 (s)	135.9 (s)	128.5 (s)	129.1 (d)	136.4 (s)	31.8 (t)	149.4 (d)	16.7 (q)
2b	187.2 (s)	132.0 (s)	129.1 (d)	129.0 (s)	135.5 (d)	136.1 (s)	16.7 (q)	147.3 (d)	17.8 (q)
cis-**2d**	186.7 (s)	134.5 (s)	126.7 (d)	129.1 (s)	134.3 (d)	146.6 (s)	16.4 (q)	147.0 (d)	35.2 (s) 29.4 (q)
trans-**2d**	186.6 (s)	137.6 (s)	133.5 (d)	129.1 (s)	128.0 (d)	143.5 (s)	16.9 (q)	147.2 (d)	34.6 (s) 29.4 (q)

[a] Multiplicity (in parentheses) deduced from DEPT spectra; $CDCl_3$ soln. at 25°.

TABLE III

^{1}H-NMR chemical shifts [ppm] of compounds **3a–h**[a]

Compound	HO-C(1)	CH_3-C(2) or CH_2-C(2) or t-Bu-C(2)	H-C(3)	CH-C(4)	H-C(5)	CH_3-C(6) or t-Bu-C(6)
3a	6.83 (s)	3.76 (s)	7.03 (d)	4.77 (s)	7.12 (d)	2.23 (s)
3b	6.88 (s)	3.78 (s)	7.03 (d)	5.0 (s)	7.15 (d)	2.25 (s)
3c	4.6 (s)	2.23 (s)	7.05 (s)	4,77 (s)	7.05 (s)	2.25 (s)
3d	4.7 (s)	2.25 (s)	7.05 (s)	5.0 (s)	7.05 (s)	2.25 (s)
3e	5.2 (s)	1.30 (s)	7.25 (s)	4.88 (s)	7.25 (s)	1.30 (s)
3f	5.25 (s)	1.30 (s)	7.25 (s)	5.08 (s)	7.25 (s)	1.30 (s)
3g	4.73 (s)	1.26 (s)	7.17 (d)	4.80 (s)	7.10 (d)	2.23 (s)
3h	4.80 (s)	1.26 (s)	7.18 (d)	5.02 (s)	7.09 (d)	2.25 (s)

[a] Assignments verified by double resonance and or nuclear Overhauser experiments (NOE); $CDCl_3$ soln. at 25°.

TABLE IV

^{13}C-NMR chemical shifts [ppm] of compounds **3a–3h**[a]

Comp.	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	CH_3-C(2) CH_2-C(2) t-Bu-C(2)	CH-C(4)	CH_3-C(6) t-But-C(6)
3a	153.5 (s)	126.2 (s)	127.5 (d)	132.0 (s)	129.9 (d)	121.9 (s)	33,3 (t)	52.8 (d)	16.1 (q)
3b	153,6 (s)	126,2 (s)	127.4 (d)	130.5 (s)	129.9 (d)	121.8 (s)	33.2 (t)	52.8 (d)	15.9 (q)
3c	151.5 (s)	122.7 (s)	127.6 (d)	131.8 (s)	127,6 (d)	122.7 (s)	15.7 (q)	52.6 (d)	15.7(q)
3d	152.5 (s)	123.5 (s)	128.3 (d)	131.1 (s)	128.3 (d)	123.5 (s)	16.3 (q)	53.3 (d)	16.3 (q)
3e	153.1 (s)	135.6 (s)	124.1 (d)	130.8 (s)	124.1 (d)	135.6	30.1 (q) 34.2 (s)	53.8 (d)	30.1 (q) 34.2 (s)
3f	153.3 (s)	135.6 (s)	124.2 (d)	129.5 (s)	124.2 (d)	135.6 (s)	30.1 (q) 34.1 (s)	53.9 (d)	30.1 (q) 34.1 (s)
3g	152.5 (s)	135.7 (s)	124.9 (d)	131.9 (s)	127.9 (d)	123.4 (s)	30.1 (q) 34.8 (s)	53.6 (d)	16.4 (q)
3h	152.9 (s)	135.9 (s)	125,2 (d)	130.7 (s)	128.1 (d)	123.6 (s)	30.1 (q) 34.9 (s)	53.9 (d)	16.4 (q)

[a] Multiplicity (in parentheses) deduced from DEPT spectra; $CDCl_3$ soln. at 25°.

TABLE V

^{1}H-NMR chemical shifts [ppm] of compounds **4a–g**[a]

Compound	CH_3-C(2) or CH_2-C(2) or t-Bu-C(2)	H-C(3)	H-C(5)	CH_3-C(6) or t-Bu-C(6)
4a	3.43 (s)	7.80 (d)	7.66 (m)	1.93 (s)
cis-**4b**[b]	3.45 (s)	7.95 (d)	7.78 (m)	2.05 (s)
trans-**4b**	3.45 (s)	7.90 (d)	7.82 (m)[c]	2.05 (s)
4c	2.05 (s)	7.80 (s)	7.80 (s)	2.05 (s)
4d	1.30 (s)	7.80 (s)	7.80 (s)	1.30 (s)
4e	1.30 (s)	7.77(d)	7.83 (d)[c]	1.30 (s)
4f	1.30 (s)	7.87 (d)	7.75 (m)	1.30 (s)
cis-**4g**[d]	1.30 (s)	7.87 (d)	7.78 (m)	2.03 (s)
trans-**4g**[d]	1.30 (s)	7.82 (d)	7.71 (m)[c]	2.03 (s)

[a] Assignments verified by double resonance and or nuclear Overhauser experiments (NOE); $CDCl_3$ soln. at 25°. [b] SCH_2COOCH_3 group *cis* to C(3); in solution isomerization to a 1:1 *cis/trans* mixture occurs. [c] cis to SCH_2COOCH_3 group. [d] data from 1:1 *cis/trans* mixture.

TABLE VI

^{13}C-NMR chemical shifts [ppm] of compounds **4a** and **4c–4e**[a]

Comp.	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	CH_3-C(2) CH_2-C(2) t-Bu-C(2)	C-C(4)	CH_3-C(6) t-But-C(6)
4a	186.9 (s)	134.3 (s)	132.3 (d)	134.9 (s)	132.0 (d)	134.9 (s)	30.7 (t)	159.3 (s)	16.6 (q)
4c	188.7 (s)	134.2 (s)	132.2 (d)	135.9 (s)	132.3 (d)	134.2 (s)	16.9 (q)	157.0 (s)	16.9 (q)
4d	187.0 (s)	146.0 (s)	128.2 (d)	135.8 (s)	128.2 (d)	146.0 (s)	29.0 (q) 34.8 (s)	154.8 (s)	29.0 (q) 34.8 (s)
4e	187.3 (s)	147.2 (s) or 147.0 (s)	128.7 (d) or 128.4 (d)	137.6 (s)	128.7 (d) or 128.4 (d)	147.2 (s) or 147.0 (s)	29.4 (q) 35.0 (s)	150.9 (s)	30.1 (q) 35.0 (s)

[a] Multiplicity (in parentheses) deduced from DEPT spectra; $CDCl_3$ soln. at 25°.

TABLE VII

^{1}H-NMR chemical shifts [ppm] of compounds **5a–5g**[a]

Compound	HO-C(1)	CH_3-C(2) or CH_2-C(2) or t-Bu-C(2)	H-C(3)	H-C(5)	CH_3-C(6) or t-Bu-C(6)
5a	6.82 (s)	3.80 (s)	7.40 (d)	7.55 (d)	2.25 (s)
5b	6.90 (s)	3.75 (s)	7.40 (d)	7.55 (d)	2.25 (s)
5c	4.60 (s)	2.25 (s)	7.45 (s)	7.45 (s)	2.25 (s)
5d	5.20 (s)	1.25 (s)	7.66 (s)	7.66 (s)	1.25 (s)
5e	5.25 (s)	1.40 (s)	7.66 (s)	7.66 (s)	1.40 (s)
5f	4.70 (s)	1.25 (s)	7.66 (d)	7.45 (d)	2.23 (s)
5g	4.85 (s)	1.40 (s)	7.65 (d)	7.46 (d)	2.20 (s)

[a] Assignments verified by double resonance and or nuclear Overhauser experiments (NOE); $CDCl_3$ soln. at 25°.

TABLE VIII

^{13}C-NMR chemical shifts [ppm] of compounds **5a–5g**[a]

Comp.	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	CH_3-C(2) CH_2-C(2) t-Bu-C(2)	C-C(4)	CH_3-C(6) t-But-C(6)
5a	153.3 (s)	125.5 (s)	128.0 (d)	133.1 (s)	130.2 (d)	121.1 (s)	30.8 (t)	73.4 (s)	16.2 (q)
5b	152.7 (s)	125.2 (s)	128.0 (d)	131.6 (s)	130.3 (d)	121.4 (s)	31.0 (t)	74.4 (s)	16.2 (q)
5c	151.5 (s)	122.2 (s)	128.3 (d)	133.0 (s)	128.3 (d)	122.2 (s)	16.0 (q)	73.3 (s)	16.0 (q)
5d	153.4 (s)	135.3 (s)	125.3 (d)	131.8 (s)	125.3 (d)	135.3 (s)	30.7 (q) 34.5 (s)	74.5 (s)	30.7 (q) 34.8 (s)
5e	153.4 (s)	135.3 (s)	124.9 (d)	130.2 (s)	124.9 (d)	135.3 (s)	30.3 (q) 34.8 (s)	75.3 (s)	30.3 (q) 34.5 (s)
5f	151.8 (s)	134.5 (s)	125.2 (d)	132.2 (s)	127.8 (d)	122.6 (s)	29.7 (q) 34.6 (s)	73.6 (s)	16.0 (q)
5g	152.1 (s)	136.3 (s)	125.1 (d)	130.8 (s)	127.9 (d)	122.4 (s)	29.5 (q) 34.6 (s)	74.6 (s)	15.9 (q)

[a] Multiplicity (in parentheses) deduced from DEPT spectra; $CDCl_3$ soln. at 25°.

TABLE IX

Mass spectra of **3c–3h**, **4a–g** and **5a–g**

Comp. [a]	$M^{+\cdot}$	Base Peak	Other Important Peaks
3c	424(0.1)	279($(M-C_8H_{17}S)^+$)	423(0.3), 311($(M-C_8H_{17})^+$, 0.3)
3d[b]	384(0.1)	279($(M-CH_3OOCCH_2S)^+$)	383(0.7), 353($(M-CH_3O)^+$, 0.5), 239($(M-C_8H_{17}S)^+$, 75))
3e	508(0.03)	363($(M-C_8H_{17}S)^+$)	507(0.1), 451($(M-C_4H_9)^+$, 0.8), 395($(M-C_8H_{17})^+$, 0.7)
3f	468(0.1)	363($(M-CH_3OOCCH_2S)^+$)	467(0.3), 411($(M-C_4H_9)^+$, 0.8), 395($(M-CH_3OOCCH_2)^+$, 1.5)
3g[b]	466(0.5)	321($(M-C_8H_{17}S)^+$)	465(2), 409($(M-C_4H_9)^+$, 0.4), 353($(M-C_8H_{17})^+$, 0.6)
3h[b]	426((0.5)	321($(M-CH_3OOCCH_2S)^+$)	425(2), 395($(M-CH_3O)^+$, 1), 353($(M-CH_3OOCCH_2)^+$, 2), 281($(M-C_8H_{17}S)^+$, 64)
4a[b]	567[c](0.9)	203	
4b[b]	527[c](1)	147	203(56)
4c	422(16)	165($(M-C_8H_{17}S-C_8H_{16})^+$)	309($(M-C_8H_{17})^+$, 7), 277($(M-C_8H_{17}S)^+$, 11)
4d	506(57)	247	491($(M-CH_3)^+$, 34), 393($(M-C_8H_{17})^+$, 13), 361($(M-C_8H_{17}S)^+$, 11), 305($(M-C_8H_{17}S-C_4H_8)^+$, 11)
4e	466(3)	247	361($(M-CH_3OOCCH_2S)^+$, 10), 321($(M-C_8H_{17}S)^+$, 10)
4f	464(43)	157	449($(M-CH_3)^+$, 51), 351($(M-C_8H_{17})^+$, 13), 319($(M-C_8H_{17}S)^+$, 7), 205(69), 191(55)
4g	424(43)	205	409($(M-CH_3)^+$, 36), 319($(M-CH_3OOCCH_2S)^+$, 44), 279($(M-C_8H_{17}S)^+$, 28)
5a[b]	712(<0.01)	147	711(0.04), 567($(M-C_8H_{17}S)^+$, 23), 203(58)
5b[b]	650(0.07)	147	649(0.2), 545($(M-CH_3OOCCH_2S)^+$, 3), 527($(M-C_6H_5CH_2S)^+$, 2), 505($(M-C_8H_{17}S)^+$, 2), 455(17), 203(90)
5c	568(0.06)	423($(M-C_8H_{17}S)^+$)	567(0.2),455($(M-C_8H_{17})^+$, 0.5), 165(96)
5d[b]	652(<0.01)	203	653[c](<0.01), 651(<0.01), 507($(M-C_8H_{17}S)^+$, 84)
5e[b]	590(<0.01)	323	591[c](0.03), 589(0.03), 485($(M-CH_3OOCCH_2S)^+$, 91), 467($(M-C_6H_5CH_2S)^+$, 33), 445($(M-C_8H_{17}S)^+$, 21), 363(91)
5f	610(0.2)	465($(M-C_8H_{17}S)^+$)	609(0.3), 553($(M-C_4H_9)^+$, 0.4)
5g	548(<0.01)	91($(C_6H_5CH_2)^+$)	547(0.08), 517($(M-CH_3O)^+$, 0.3), 443($(M-CH_3OOCCH_2S)^+$, 24), 425(($M-C_6H_5CH_2S)^+$, 35), 403($(M-C_8H_{17}S)^+$, 15), 207(77)

[a] EI [b] CI [c] $(MH)^+$

exocyclic C,C double bond was discussed by Rieker.[4] The ^{13}C-NMR resonances of the carbonyl group in **4a–g** were detected in the expected range between 186 and 189 ppm, similarly to that observed for **2a**[1]; the resonances of the terminal carbon of the C═C—C═C—C═O moiety are shifted downfield as compared to the corresponding resonance in **2a**[1] (Table VI). The red-orange compounds **4a–g** show a typical UV absorption maximum at 389–409 nm in acetonitrile (cf. Reference 5); one or two IR absorptions were found for the C═C—C═C—C═O moiety between 1595 and 1655 cm^{-1} (see Experimental part).[6] Mass spectra, see Table IX.[7]

Synthesis of compounds **3a–h** and **4a–g** represents a simple and straightforward access to *p*-hydroxybenzaldehyde dithioacetals and 7,7-bis(alkylthio)-*p*-quinone methides, respectively, with two different sulfur substituents.

SYNTHESIS OF TRITHIO-ORTHOBENZOATES **5a–g**

The compounds **4a–g** constitute synthetic equivalents of α,α-bis(alkylthio)-4-hydroxybenzylcations **Cb**. Addition of thiols R^{4}SH in boiling hexane solution under analogous conditions (see above) affords the trithio-orthobenzoates **5a–g** in yields between 44 and 99%. The ^{1}H and ^{13}C chemical shift values of **5a–g** are in good agreement with the proposed structures (Tables VII and VIII). The quaternary carbon linked to three alkylthio substituents shows a typical absorption between 73 and 76 ppm in the ^{13}C-NMR spectrum. Some of the compounds **5a–g** also required the DCI technique for molecular mass confirmation. The expected typical fragmentations of the alkylthio radicals linked to C(7) were observed in all cases; if all side chains RS are identical, this fragmentation predominates (see Table IX).

DISCUSSION

The synthetic sequence **1** → **2** → **3** → **4** → **5** opens a simple access to *p*-hydroxytrithio-orthobenzoates with three different sulfur substituents. In particular, it does not require strongly basic conditions,[8] which are very often not compatible with several functional groups also present in the molecule. In contrast to another method recently reported for the synthesis of trithio-orthoformates,[9] in the oxidation step **3** → **4** no strict exclusion of water is necessary and no isolation and purification of the intermediate **4** is required. The synthesis is compatible with other oxidizable functional groups linked to the phenolic moiety such as *ortho*-alkylthiomethyl groups.

EXPERIMENTAL

General: cf. Reference 1. ^{1}H-NMR in $CDCl_3$. UV-spectra in acetonitrile, λ_{max} (logϵ) in nm. TLC: silica gel; R_f values for hexane/AcOEt 9:1 (A).

4-Hydroxybenzylthioethers **1a–d**: **1a**[1]; **1c**[10]; **1b** and **1d** were synthesized according to the procedure described in Reference 10. *2,6-Dimethyl-4-octylthiomethylphenol* (**1b**), yellowish liquid, yield 99.5%, R_f (A): 0.30. ^{1}H-NMR: 7.25 (s, 2H, aromat. H), 4.56 (s, 1H, OH), 3.59 (s, 2H, Ar—CH_2—S), 2.42 (t, J = 7.5, 2H, S—CH_2—CH_2—), 2.22 (s, 3H, Ar—CH_3), 1.56 (quintet, J = 7.5, 2H, S—CH_2—CH_2—), 1.4–1.2 (m, 10H), 0.88 (t, J = 7, 3H, CH_3—CH_2—). Anal. calc. for $C_{17}H_{28}OS$ (280.45): C 72.80, H 10.06, S 11.43; found: C 72.67, H 10.10, S 11.57.

2-t-Butyl-6-methyl-4-octylthiomethylphenol (**1d**), yellowish liquid, yield 74.4%. B.p. 140–142°/0.006 mbar, R_f (A): 0.46. ^{1}H-NMR: 7.05 and 6.96 (2 br. s, 2H, aromat. H), 4.69 (br. s, 1H, OH), 3.62 (s, 2H, Ar—CH_2—S), 2.42 (t, J = 7.5, 2H, S—CH_2—CH_2—), 2.22 (s, 3H, Ar—CH_3), 1.56 (quintet, J = 7.5,

2H, S—CH_2—CH_2—), 1.40 (s, 9H, t-But-Ar), 1.4–1.2 (m, 10H), 0.88 (t, J = 7, 3H, CH_3—CH_2—). Anal. calc. for $C_{20}H_{34}OS$ (322.55): C 74.48, H 10.63, S 9.94; found: C 74.49, H 10.86, S 9.98.

Monosubstituted quinone methides **2a–d**: **2a**[1]; **2b–d** were prepared according to the procedure described in Reference 1; ^{1}H-NMR and ^{13}C-NMR spectra see Tables I and II.

2,6-Dimethyl-4-[(octylthio)methyliden]cyclohexa-2,5-dien-1-one (**2b**), red orange resin, yield 99.6%, purity 98.7% (HPLC). M.p. 37.9° (DSC), R_f (A): 0.42. UV: 382 (4.30). IR ($CHCl_3$): 1634 (C=O), 1599 (C=C). Anal. calc. for $C_{17}H_{26}OS$ (278.45): C 73.33, H, 9.41, S 11.51; found: C 73.03, H 9.52, S 11.86.

2,6-Di-t-butyl-4-[(octylthio)methyliden]cyclohexa-2,5-dien-1-one (**2c**), orange resin, yield M.p. 37.1°C (DSC), R_f (A): 0.86. UV: 377 (4.59). IR (KBr): 1633. ^{1}H-NMR: Anal. calc. for $C_{23}H_{38}OS$ (382.62): C 76.18, H 10.56, S 8.84; found: C 76.24, H 10.67, S 9.01.

2-t-Butyl-6-methyl-4-[(octylthio)methyliden]cyclohexa-2,5-dien-1-one (**2d**), red liquid, yield 99.4%, R_f (A): 0.50. UV: 380 (4.53). IR (KBr): 1631 (C=O), 1592 (C=C). Anal. calc. for $C_{20}H_{32}OS$ (320.54): C 74.94, H 10.06, S 10.00; found: C 74.90, H 10.08, S 10.28.

Dithioacetals **3a–h**: **3a** and **3b**[1]; general procedure for preparation of **3c–h**: 0.1 mol of a thiol is added to a solution of 0.1 mol of the quinone methide **2** and 10 mol% triethylamine (method A) in 150–300 ml hexane or to a two phase system of 0.1 mol of quinone methide **2** in 150–300 ml hexane and 250 mol% 1N NaOH (method B) and stirred at 65° under reflux. The organic phase is separated and dried (method B) and evaporated at 70°/0.006 mbar. The product can be further purified by flash chromatography (FC); ^{1}H-NMR and ^{13}C-NMR spectra see Tables III and IV; mass spectra see Table IX.

4-[Bis(octylthio)methyl]-2,6-dimethylphenol (**3c**): 5 h (A); yellowish oil, yield 100%; R_f (A): 0.41. Anal. calc. for $C_{25}H_{44}OS_2$ (424.80): C 70.70, H 10.44, S 15.10; found: C 70.70, H 10.44, S 14.80.

2,6-Dimethyl-4-[[(methoxycarbonyl)methylthio](octylthio)methyl]phenol (=Methyl[[4-Hydroxy-3,5-dimethylphenyl](octylthio)methylthio]acetate; **3d**), 3 h (A); colorless oil, yield 66.2% (FC: hexane/toluene 49:1), R_f (A): 0.19. IR (KBr): 1732 (C=O). Anal. calc. for $C_{20}H_{34}OS$ (384.59): C 62.46, H 8.39, S 16.67; found: C 62.57, H 8.41, S 16.75.

4-[Bis(octylthio)methyl]-2,6-di-t-butylphenol (**3e**), 8h (B); yellowish oil, yield 95.9% (FC: hexane/toluene 49:1); R_f (A): 0.91. Anal. calc. for $C_{31}H_{56}OS_2$ (508.91): C 73.16, H 11.09, S 12.60; found: C 73.33, H 10.85, S 12.36.

2,6-Di-t-butyl-4-[[(methoxycarbonyl)methylthio](octylthio)methyl]phenol (=Methyl[[4-Hydroxy-3,5-di-t-butyl-phenyl](octylthio)methylthio]acetate; **3f**), 2 h (A); yellow oil, yield 99.8%; R_f (A): 0.57. IR (KBr): 1737 (C=O). Anal. calc. for $C_{26}H_{44}O_3S_2$ (468.75): C 66.62, H 9.46, S 13.68; found: C 66.96, H 9.50, S 13.60.

4-[Bis(octylthio)methyl]-2-t-butyl-4-methylphenol (**3g**), 5.5 h (A); yellow oil, yield 86.4% (FC: hexane/EtOAc 23:2); R_f (A): 0.49. Anal. calc. for $C_{28}H_{50}OS_2$ (466.83): C 72.04, H 10.80, S 13.74; found: C 72.01, H 10.79, S 13.63.

2-t-Butyl-4-[[(methoxycarbonyl)methylthio](octylthio)methyl]-6-methylphenol (=Methyl[[4-Hydroxy-3-t-butyl-5-methyl-phenyl](octylthio)methylthio]acetate; **3h**), 2 h (A); yellow oil, yield 93.4%; R_f (A): 0.24. IR (KBr): 1733 (C=O). Anal. calc. for $C_{23}H_{38}O_3S_2$ (426.67): C 64.75, H 8.98, S 15.03; found: C 64.97, H 9.10, S 14.84.

Disubstituted quinone methides **4a–d** were prepared according to the procedure described for **2a**[1]; ^{1}H-NMR and ^{13}C-NMR spectra see Tables V and VI; mass spectra see Table IX.

4-[Bis(octylthio)methyliden]-2-methyl-6-(octylthio)methylcyclohexa-2,5-dien-1-one (**4a**), red orange resin, yield 96.2%. M.p. 35.8° (DSC), R_f (A): 0.61. UV: 408 (4.46). IR ($CHCl_3$): 1623 (C=O). Anal. calc. for $C_{33}H_{58}OS_3$ (567.01): C 69.90, H 10.31, S 16.96; found: C 69.61, H 10.40, S 16.81.

4-[[(Methoxycarbonyl)methylthio] (octylthio)methyliden]]-2-methyl-6-(octylthio)methylcyclohexa-2,5-dien-1-one [=Methyl {[4-Hydroxy-3-methyl-4-(octylthio)methylphenyl](octylthio)methylidenthio}acetate; **4b**), red liquid, yield 90.3%; R_f (A): 0.27. UV: 400 (4.15). IR ($CHCl_3$): 1742 (C=O), 1654 (C=O). Anal. calc. for $C_{28}H_{46}O_3S_3$ (526.87): C 63.83, H 8.80, S 18.26; found: C 63.69, H 8.83, S 17.83.

2,6-Dimethyl-4-[bis(octylthio)methyliden]cyclohexa-2,5-dien-1-one (**4c**), red orange resin, yield 99.1%; R_f (A): 0.48. UV: 403 (4.43). IR (KBr): 1630 (C=O), 1608 (C=C). Anal. calc. for $C_{25}H_{42}OS_2$ (422.80): C 71.03, H 10.01, S 15.17; found: C 71.06, H 10.08, S 15.00.

2,6-Di-t-butyl-4-[bis(octylthio)methyliden]cyclohexa-2,5-dien-1-one (**4d**), orange oil, yield 100%, R_f (A): 0.91. UV: 400 (4.44). IR (KBr): 1624 (C=O). Anal. calc. for $C_{31}H_{54}OS_2$ (506.94): C 73.46, H 10.74, S 12.65; found: C 73.49, H 10.78, S 12.47.

2,6-Di-t-butyl-4-[[(methoxycarbonyl)methylthio](octylthio)methyliden]]cyclohexa-2,5-dien-1-one (=Methyl {[2,6-di-t-butyl-4-hydroxyphenyl]-(octylthio)methylidenthio}acetate; **4e**), red orange oil, yield 97.7%; R_f (A): 0.55. UV: 389 (4.41). IR ($CHCl_3$): 1743 (C=O), 1655 (C=O). Anal. calc. for $C_{26}H_{42}O_3S_2$ (466.47): C 66.91, H 9.07, S 13.74; found: C 67.63, H 9.33, S 13.48.

2-t-Butyl-6-methyl-4-[bis(octylthio)methyliden]cyclohexa-2,5-dien-1-one (**4f**), orange oil, yield 99.3%; R_f (A): 0.57. UV: 401 (4.42). IR (KBr): 1610 (C=O), 1594 (C=C). Anal. calc. for $C_{28}H_{48}OS_2$ (464.81): C 72.35, H 10.41, S 13.79; found: C 72.59, H 10.35, S 13.75.

2-t-Butyl-4-[[(methoxycarbonyl)methylthio](octylthio)methyliden]]-6-methylcyclohexa-2,5-dien-1-one (= Methyl[[2-t-butyl-4-hydroxy-6-methylphenyl]-(octylthio)methyliden-thio]acetate; **4g**), red orange oil, yield 97.9%; R_f (A): 0.28. UV: 394 (4.32). IR ($CHCl_3$): 1742 (C=O), 1611 (C=O). Anal. calc. for $C_{23}H_{38}O_3S_2$ (424.66): C 64.75, H 8.98, S 15.03; found: C 64.97, H 9.10, S 14.84.

The trithio-orthoesters **5a–g** were prepared according to the procedure described for **3c–h**; ^{1}H-NMR and ^{13}C-NMR spectra see Tables VII and VIII; mass spectra see Table IX.

Trioctyl 4-hydroxy-3-methyl-5-(octylthio)methyl-trithio-orthobenzoate (**5a**), 6 h (B), yield 84.6% (FC hexane/EtOAc 49:1), red orange oil, yield 97.7%; R_f (A): 0.82. Anal. calc. for $C_{41}H_{76}OS_4$ (713.30): C 69.04, H 10.74, S 17.98; found: C 69.00, H 10.81, S 17.88.

Benzyl-[(methoxycarbonylmethyl)thio]methyl-octyl 4-hydroxy-3-methyl-5-(octylthio)methyl-trithio-orthobenzoate (**5b**), 3 h (25°; method B); orange resin, yield 43.7% (FC hexane/EtOAc 19:1); R_f (A): 0.37. IR (KBr): 1741 (C=O). Anal. calc. for $C_{35}H_{54}O_3S_4$ (651.08): C 64.57, H 8.36, S 19.70; found: C 64.63, H 8.45, S 19.46.

Trioctyl 3,5-dimethyl-4-hydroxy-trithio-orthobenzoate (**5c**), 18 h (B); reddish oil, yield 99.3% (FC hexane/EtOAc 49:1); R_f (A): 0.51. Anal. calc. for $C_{33}H_{60}OS_3$ (569.03): C 69.66, H 10.63, S 16.90; found: C 69.79, H 10.68, S 16.79.

Trioctyl 3,5-di-t-butyl-4-hydroxy-trithio-orthobenzoate (**5d**), 36 h (B, +2 mol% benzyltributylammonium chloride); red orange oil, yield 75.1% (FC hexane and hexane/toluene 9:1); R_f (A): 0.87. Anal. calc. for $C_{39}H_{72}OS_3$ (653.18): C 71.71, H 11.11, S 14.72; found: C 71.51, H 11.19, S 15.08.

Benzyl-[(methoxycarbonylmethyl)thio]methyl-octyl 3,5-di-t-butyl-4-hydroxy-trithio-orthobenzoate (**5e**), 6 h (A); yellow oil, yield 56.2% (FC hexane/EtOAc 49:1); R_f (A): 0.42. IR (KBr): 1746 (C=O). Anal. calc. for $C_{33}H_{50}O_3S_3$ (590.94): C 67.07, H 8.53, S 16.28; found: C 66.80, H 8.62, S 16.20.

Trioctyl 3-t-butyl-4-hydroxy-5-methyl-trithio-orthobenzoate (**5f**), 17 h (B); red orange oil, yield 97.5%; R_f (A): 0.59. Anal. calc. for $C_{36}H_{66}OS_3$ (611.10): C 70.76, H 10.89, S 15.74; found: C 70.87, H 10.79, S 15.67.

Benzyl-[(methoxycarbonylmethyl)thio]methyl-octyl 3-t-butyl-4-hydroxy-5-methyl-trithio-orthobenzoate (**5g**), 2 h (A); yellow oil, yield 47.3% (FC hexane/EtOAc 9:1); R_f (hexane/AcOEt 19:1): 0.26. IR (KBr): 1739 (C=O). Anal. calc. for $C_{30}H_{44}O_3S_3$ (548.87): C 65.65, H 8.08, S 17.52; found: C 65.70, H 8.34, S 17.50.

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