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ORIGINAL PAPER

Synthesis and Antioxidancy of Some *n*-Alkyl, *t*-Alkyl, Homologous and Isomeric Lipidic Alkylthiobisphenols

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Abstract To study the relationship between structure and properties of members of the lipidic thiobis phenol series, as extreme pressure additives in lubricants, a series of homologous compounds has been synthesised by the reaction of alkylphenols with sulphur dichloride. The isomeric *n*-nonylphenols have been reacted to form the C9 isomeric 2,2′-and 4,4′-thiobisphenols. Longer alkyl side-chains resulted mainly in the formation of 4,4′-thiobisphenols and some of the 2,2′ isomer. With short alkyl, particularly *t*-alkyl side-chains, steric hindrance resulted in the 2,2′-compound. Additive studies have indicated that the longer chain 4,4′ compounds possessed antioxidant properties comparable and superior to former commercial branched chain 2,2′ compounds produced from petrochemical intermediates.

Keywords Thiobisphenols · Lubricating oils · Antioxidancy

Introduction

Lipidic compounds have had a significant role particularly under boundary or extreme pressure conditions over many years as lubricant additives [1]. Traditionally, compounds containing sulphur, such as thiobisphenols [2] have been derived from 4-*t*-nonylphenol. More recently, compounds with multi-functional properties containing both sulphur and phosphorus, e.g. alkyldithiophosphates [3], the phosphorodithioates [4] have been developed and structure/properties investigated. The use of additives from natural products has been reviewed [5]. Previously, [6] the syntheses of a series of thiobisphenols were described by reaction with sulphur dichloride, from 3-alkylphenols obtained from renewable, natural phenolic lipid sources [7, 8], having saturated C_8, C_{11} and C_{15} side chains. However, to our knowledge, there has been no study of the relationship between structure and properties in such thiobisphenols.

This present communication is concerned with this aspect. Some of the products synthesised from natural resources possessed additive properties comparable with the commercial thiobisphenols, obtained from 4-*t*-nonylphenol (**10**, R = *t*-C_9 H_{19}) and (**10**, R = *t*-C_8H_{17}). The use of these compounds seems to have been due to the derivation and absence of isomer formation rather than from a structure/property study. In the present paper we describe syntheses of a range of compounds with different *n*-alkyl chain lengths, branching, isomeric positions of the *n*-alkyl group in the aryl ring and of certain *n*-pentadecyl compounds bearing unsaturation. 3-Alkylphenols are readily accessible only from natural resources and their 2-and 4-alkyl isomers in the present work by synthesis from *n*-alkanoic sources as studied in the aldoxime series [9]. Surfactant compounds with *n*-alkyl chains are more biodegradable than those with branched chains [10] and it seems likely that the same probability applies to sulphur analogues.

The role of structure and properties in the thiobisphenol series may be of general interest in other areas of biology/technology. These compounds have a variety of other uses, for example as UV absorbers in polymers [11], coking inhibitors in diesel fuels [12] and as antioxidants and metal deactivators [13].

Lipidic alkylthiobisphenols: Long chain phenols, Part 40b (Part 40a, ref 6).

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Experimental Procedures

Materials

2-*n*-, 3-*n*- and 4-*n*-Nonylphenols were synthesised by the reaction of 2-hydroxybenzaldehyde (salicyl aldehyde), 3-hydroxybenzaldehyde and 4-hydroxybenzaldehyde with *n*-octyltriphenylphosphonium bromide prepared from the requisite bromoalkane with triphenylphosphine, respectively by the Wittig reaction as described [14]. 3-Undecylphenol is available from *Anacardium giganteum* [7], but was also synthesised from 1-decylphosphonium bromide and 3-hydroxybenzaldehyde. Reduction of the resultant alkenes from the Wittig reaction [14], by catalytic hydrogenation, gave the required alkylphenols. 2- and 4-Alkylphenols were obtained by Fries rearrangements of phenyl esters (from phenol and *n*-alkanoic acids) to give the ketoalkyl intermediates which were reduced to give the 2- and 4-*n*-alkylphenols [9]. 2-(1,1,3,3-tetramethylbutyl) phenol was obtained by a described procedure [15].

Cashew nut shell liquid was obtained from 3M Research (Harlow, Essex, UK). Cardanol monoene was obtained by the catalytic hydrogenation of mixed cardanol in ethanol containing Raney nickel or by chemical reduction [9] and mixed cardanol by the base addition method [7] and vacuum distillation. Saturated cardanol (3-pentadecylphenol was prepared by catalytic hydrogenation with a Pd/C catalyst and by chemical reduction of mixed cardanol with hydrazine/air [7]. Sulphur dichloride was purified as described [6]. Other chemicals were obtained from Aldrich Chemical Co. Ltd.

Chromatography and Spectroscopy

Chromatography: Column chromatography, TLC and PLC were carried out with silica gel as described [6].

Spectroscopy (IR, NMR, MS) was effected by the procedures described [6].

Synthesis of Thiobisphenols

2,2′and 4,4′-thiobisphenols were prepared by a general procedure:

The alkylphenol (0.10 mol) in solvent (chloroform, acetonitrile, benzene, or hexane) (as indicated in Table 1), (125 cm^3) cooled to 0 °C was treated under nitrogen with sulphur dichloride (0.055 mol) in the same solvent

Table 1 Synthesis of thiobisphenols (TBS)

ArOH			TBS synthesis		TBS												Sepn·
					2,2′ product						4,4′ product						
Reactant	R	R_f	Solvent	Cat.	No.	R	Mp (°C)	R_f	% yield	M$^+$	No.	R	Mp (°C)	R_f	% yield	M$^+$	
1	Me	0.53	B	–	3	Me	–	–	–	–	2	Me	128–130[20]	0.16	27	246.6081[b]	C
1	Et	0.51	C	–	3	Et	Oil	0.53	25.6	–	2	Et	Oil	0.11	59.5	274.1[c]	GE
1	n-Pr	0.64	C	–	3	n-Pr	–	–	–	–	2	n-Pr	Oil	0.23	51	302.1[d]	GE
1	n-Bu	0.55	C	–	3	n-Bu	Oil	0.62	7.1	–	2	n-Bu	Oil	0.12	41.6	330.1829[e]	CC
1	t-Bu[a]	0.72	C	–	3	t-Bu	169–172	0.80	44.8	–	2	t-Bu	Nil	–	–	–	C
5	n-C9	0.69	C	–	7	n-C9	Oil	0.72	–	–	6	n-C9	Oil	0.24	44.5	470.0[f]	FC/PLC
1	n-C9	0.56	A	Fe	3	n-C9	Oil	0.60	11.1	470.3	2	n-C9	Oil	0.26	66.6	470.3[g]	CC
9	n-C9	0.67	C	–	10	n-C9	Oil	0.73	59.1	470.3380	–	Nil	Nil	Nil	Nil	Nil	PLC
5	t-C8	0.85	H.	Fe	7	t-C8	–	–	–	–	6	t-C8	Oil	0.35	67.9	442.3[h]	PLC
1	n-C11	0.57	C	–	3	n-C11	Oil	0.66	14.1		2	n-C11	Oil	0.22	39.6	526.3[i]	GE
1	n-C15	0.60	B[6]	–	3	n-C15	53–55	0.69	14.1	638.5090	2	n-C15	77–79	0.33	27.9	638.5[j]	FC

Numbering of compounds as in Schemes 1, 2 and 3

[a] Found: C, 72.48; H, 7.93. Reqd.: C, 72.68; H, 7.93%

[b] Reqd.: 246.6088

[c] 274.1022

[d] 302.1344

[e] 330.1824

[f] 470.0

[g] 470.3

[h] 442.2894

[i] 526.3830

[j] 638.5090

(50 cm^3) over 60 min. The mixture was allowed to warm to ambient temperature (TLC monitoring, $CHCl_3$:EtOAc, 95:5) and maintained at that temperature until TLC indicated absence or a reduced amount of the starting material. The mixture was concentrated in vacuo and the residue separated by, crystallisation for solids (C), or by column chromatography (CC), with gradient elution (GE), flash chromatography (FC), or preparative TLC (PLC) for oils, as indicated in Table 1. GE and FC were conducted with chloroform/ethyl acetate mixtures, PLC with light petroleum/diethyl ether (80:20).

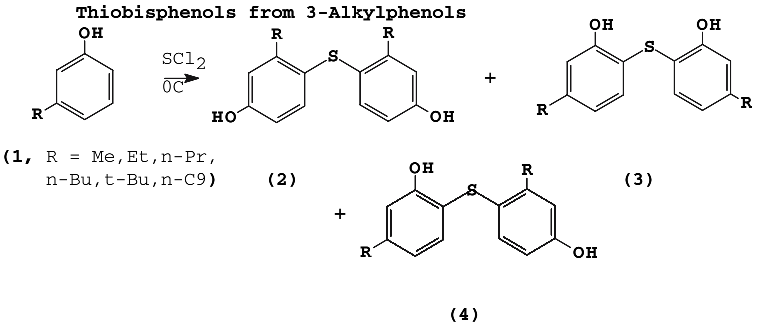
Evaluation of 2,2′and 4,4′-Thiobisphenols by Antioxidancy and Corrosion Tests

For these tests, samples were prepared containing the respective thiobisphenol additive (0.42 g), a dispersant16 (0.45 g) and Marcol 172 to make 30.0 g of a mixture. (Marcol 172 is a refined lubricating white oil and the dispersant was based on an alkenylsuccinic anhydride reacted with a polyamine). Thus, the thiobisphenols in Schemes 1, 2 and 3, (**2**, R = *n*-$C_{15}H_{31}$), (**2**, R = *n*-C_9H_{19}), (**6**, R = *t*-C_8H_{17}), (**6**, R = *n*-C_9H_{19}), (**10**, R = *n*-C_9H_{19}) and [6], the reference compound (**10**, R = *t*-C_8H_{17}) were examined by comparison with a control sample without additive. The C15 compound in the present test series was a technical unseparated sample containing the 4,4′ (65%) and 2,2′ (30%) isomers.

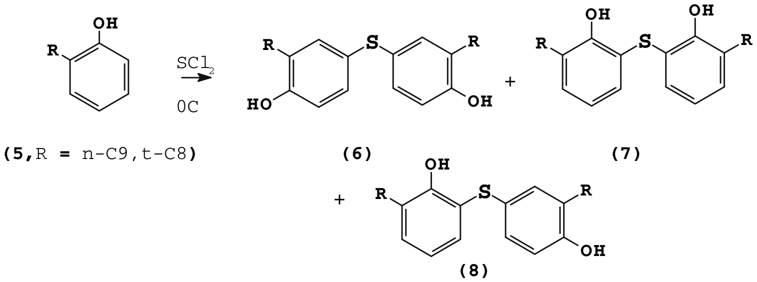
Antioxidancy Compounds were examined in an oxidative environment. The dynamic viscosities of test samples removed from the series at 165 °C, were determined after 64 h duration and compared, on a HAAKE viscometer PK100, thermostat bath K15, controller D3 and head VT550. If the increase in viscosity was severe the run was terminated earlier as shown in Table 2.

Corrosion The test method measured the tarnish/corrosiveness of the sample to a copper strip (ASTM D 130). All samples were compared at equal mass of additive. A polished copper strip was immersed in a specific volume (30 cm^3) of the test sample for a specified duration and temperature (100 °C) at the end of which, the copper strip was removed, washed and the tarnish level assessed against

Scheme 1 Thiobisphenols from 3-alkylphenols



Scheme 2 Thiobisphenols from 2-alkylphenols



Scheme 3 Thiobisphenols from 4-alkylphenols

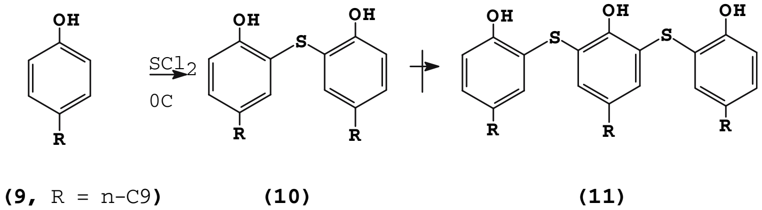


Table 2 Antioxidancy and corrosion evaluation of synthetic 4.4′- and 2,2′-thiobisphenols

Structure	Type	Viscosity (centipoises) (at 64 h)[a]	Corrosion/tarnish (Scale 1a–4d)
2; R = n-C_9H_{19}	4,4′-thiobisphenol	57.9	3a
6; R = t-C_8H_{17}	4,4′-thiobisphenol	97.2	1b
2; R = n-$C_{15}H_{31}$ (65%)	4,4′-thiobisphenol	150.7	2c
10; R = n-C_9H_{19}	2,2′-thiobisphenol	157.1	4a
6; R = n-C_9H_{19}	4,4′-thiobisphenol	300 (16 h)	3b
10;R = t-C_8H_{17}	2.2′-thiobisphenol	300 (40 h)	1b

[a] Average control value at time 0 h, 121.2 centipoises

the ASTM copper strip corrosion standard. The classification ratings are 1 (slight tarnish), 2 (moderate tarnish), 3 (dark tarnish) 4 (corrosion), with sub gradations, a, b, c and d, from better to worse respectively, within each category.

Results and Discussion

Synthesis of Thiobisphenols (Schemes 1, 2 and 3)

With 3-alkylphenols, it had been found [6] that polar solvents and a catalyst both promoted the formation of the 4,4′ rather than the 2,2′ isomer. Thus, such conditions led to a product ratio (4,4′/2,2′) of nearly 6:1. Reaction was confined to formation of only bis-thio phenols without oligomers. Thus, in Scheme 3, compound **11** did not appear to result.

In the present work, a polar solvent and the use of catalysts gave similar results as found previously [6] although these conditions were not always used so as to obtain high quantities of both isomeric products. Thiobisphenol formation occurs by way of intermediate isomeric sulphenyl chlorides [6] $RC_6H_3OH(SCl)$, to give symmetrical compounds of type 2 and 3, and there is chromatographic evidence for a very minor unsymmetrical isomer 4.

The isomeric products possessed very similar spectroscopic properties, except where hydrogen bonding occurred in *ortho* compounds, which resulted in a lower field chemical shift for the OH group in the proton NMR spectrum and a reduced $\nu_{\max}$ in the infrared spectrum. Their chromatographic behaviour was however, markedly different. Thus, the 4,4′-products all possessed lower R_f values compared to the 2,2′ isomers as with the *n*-octyl and *n*-pentadecyl compounds described [6]. This was attributed to lack of hydrogen-bonding of the OH group to the sulphur atom. Generally in this series, the sequence in TLC of R_f values was 2,2′- > precursor phenol > 4,4′-compound, while traces of two sulphenyl intermediates were located near the respective thiobisphenol isomer. R_f values of 2-alkylphenols and their thiobisphenol products were always greater than those of isomeric materials [17].

Substitution by sulphur dichloride in compounds with long *n*-alkyl side chains mainly occurred *o*- to the long *n*-alkyl chain to give the 4,4′-thiobisphenol as the major product. By contrast, steric hindrance prevented *o*-substitution to the *t*-butyl group. 3-*n*-Propyl and 3-*n*-butylphenols afforded mainly 4,4′-products with little or no 2,2′-isomer, but exceptionally, 3-ethylphenol appeared to resemble the long chain *n*-alkylphenols in giving similar proportions of the two isomers.

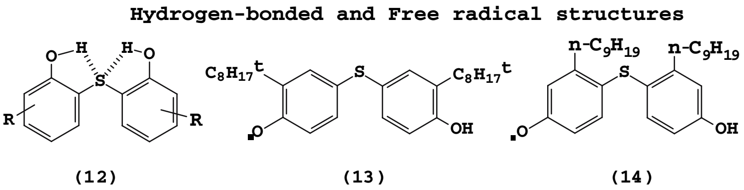
The compounds prepared by the general method and their physical properties are summarised in Table 1.

The new compounds synthesised and characterised were: di-(2-ethyl-4-hydroxyphenyl)-sulphide (**2**; R = Et); di-(4-hydroxy-2-*n*-propylphenyl)-sulphide, (**2**; R = *n*-Pr); di-(4-*t*-butyl-2-hydroxyphenyl)-sulphide (**2**; R = *t*-Bu); di-(2-*n*-butyl-4-hydroxyphenyl)-sulphide, (**2**; R = *n*-Bu); di-(4-hydroxy-2-*n*-nonylphenyl)-sulphide (**2**; R = *n*-nonyl); di-(4-hydroxy-3-*n*-nonylphenyl)-sulphide (**6**; R = *n*-nonyl); di-(2-hydroxy-5-*n*-nonylphenyl)-sulphide) (**10**; R = *n*-nonyl); di-(4-hydroxy-2-*n*-undecylphenyl)-sulphide (**2**; R = *n*-undecyl).

Physical Evaluations (Names and Formulae in Schemes 1, 2 and 3)

Increased oxidation of the test sample gave increased viscosity [18] compared to the control and effective thiobisphenol antioxidant additives led to only slightly higher, constant or even lower values. The properties of a range of six compounds tested in the viscosity and corrosion test programme are listed in Table 2 which gives the change in viscosity in centipoises over 64 h compared with the control and the colour changes found in the corrosion test. The average viscosity value for the control and control with additive at time 0 was 121.2 centipoises. In evaluations of compounds, for antioxidancy, preliminary results had indicated that compounds with short *n*-alkyl chains were not as effective as those with a longer alkyl chain. In the C15 series, the properties of the 4.4′-thiobisphenol (**2**, R = *n*-$C_{15}H_{31}$) were comparable to commercial additives

Scheme 4 Hydrogen-bonded and free radical structures



such as (**10,** R = *t*-C9), and the 2,2′-isomer was less effective, (**3,** R = *n*-$C_{15}H_{31}$).

Table 2 indicates that in terms of antioxidant ability, the 4,4′-thiobisphenols (**2,** R = *n*-C9) and (**6**, R = *t*-octyl) appeared to be more effective antioxidants than the commercial 2.2′-product **10** (R = *t*-C_8H_{17}), while notably (**6**, *n*-C_9H_{19}), was less effective. In tarnish/corrosion testing, only **6** (R = *t*-C_8H_{17}) and **10** (R = *t*-C_8H_{17}) gave corrosion-free results. In the *n*-alkyl series, a peak action for antioxidancy may occur in the middle of the range, around C9. With the *n*-C9 isomer series, the order of antioxidant activity is 3- (**2**) > 4- (**10**) > (**6**), 2-alkyl substitution.

In tarnish/corrosion testing, the order of isomer activity is different. Instability of (**2**, R = *n*-C9), to the test conditions may be involved, namely that of the C-S bond, perhaps due to some loss of coplanarity and cleavage. Generally, in this test, *n*-alkyl 4,4′-thioibisphenols were less effective than branched alkyl chain thiobis compounds.

Thus, by contrast, the 4,4′-thiobisphenol **6**, (R = *t*-octyl, 2-(1,1,3,3-tetramethyl)-butyl), possessed both effective antioxidant and anticorrosion properties. Branched chain structures appear more effective than the *n*-alkyl.

The antioxidancy results can be partly interpreted in terms of current theory that effective compounds (AH) provide a source of stable free radicals (A•) by the reaction, AH + R• = RH + A• and act as radical scavengers in the system.

2,2′-Thiobis phenols do not form radicals so readily as their 4,4′ isomers because of intramolecular hydrogen-bonding, impeding removal of the hydrogen atom as seen in the structure (**12**) (Scheme 4).

However, compounds **6**, (R = *t*-C_8) and **2**(R = *n*-C_9) can give radicals (**13**) and (**14**), (Scheme 4) notably in (**13**) due to steric stabilisation [19], as in 2,6-di-*t*-butyl-4-methylphenol (BHT).

A large number of canonical structures are possible, enhanced by the S atom, which can enlarge its normal electronic octet to twelve. Radical (**13**, R = *t*-C8), is more stable than (**14**, **R** = *n*-C_9), in the same way that 4-methyl-2,6-di-*t*-butylphenol provides a more stable radical than 2-methylphenol. The radical in (**2**, R = *n*-C_9) can be depicted in an equal number of resonant structures, although its stability is lessened compared with the branched *t*-C_8 chain. An equal number of resonant structures can be depicted for the other ring in this series of compounds and, moreover, diradical formation is possible.

Antioxidancy and corrosion tests are practical evaluatory tests, but the orientation of the lipidic chains in the thiobisphenol molecule at a metal surface may also be significant. X-ray structural information on certain of the 4.4′-thiobisphenols could be informative, but suitable crystals for this determination could not be prepared.

Although *n*-alkyl-4,4′-thiobisphenols, available from intermediates from natural sources, have useful antioxidancy but rather less effective corrosion resistance, they have potentially greater biodegradability [10] compared to 4,4′-branched chain compounds from petrochemical C8 and C9 intermediates. These, by contrast, afford radical stability, as with the ''hindered'' phenols, resulting in antioxidant ability and they also provide good corrosion resistance.

Thiobisphenols have useful properties other than as lubrication additives; for example as fungicides and bactericides [20].

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