

SYNTHESIS OF METHYL ETHERS OF ALKYLIDENEBISPHENOLS AND THIOBISPHENOLS

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17 ethers of alkylidenebisphenols and thiobisphenols were synthesized for the investigation of antioxidative properties.

Owing to a modification of the hydroxy groups, ethers and partial ethers of selected alkylidenebisphenols and thiobisphenols have a partially or completely limited ability to react with alkylperoxyls which are an important radical intermediate in the propagation step of chain autoxidation. Therefore, a further mechanism of inhibitive action can become operative in the inhibition process. For this investigation we prepared a number of ethers and partial ethers of alkylidenebisphenols and thiobisphenols, so far not described in the literature. In view of the purposes of their application, the procedure for preparation of the individual compounds was not optimized with respect to the yield.

Ethers and partial ethers of bisphenols were obtained by alkylation of phenols with dimethyl sulphate in an alkaline medium. The result of the reaction is affected by the ratio of reacting components and reaction time. Conditions suitable for the isolation of the desired product were determined by following changes in the composition of the reaction mixture by TLC. The reaction was stopped after formation of a sufficient amount of partial ether or when it had been completed. In most cases the products were isolated from the reaction mixture by elution column chromatography with a suitable system of solvents. In some cases the crystalline compound was isolated from the extract of the reaction mixture, and the mother liquors were subsequently separated by column chromatography.

Some of the required compounds could not be isolated in the pure state. For instance, ether and partial ether of 2,2'-benzylidenebis(4-methyl-6-tert-butylphenol) could not be separated even by using the chromatographic method. Therefore, alkylation of the initial bisphenol with a large excess of dimethyl sulphate yielded only 2,2'-benzylidenebis(4-methyl-6-tert-butylanisole). Also, only 4,4'-thiobis(2-methyl-6-tert-butylanisole) could be obtained from 4,4'-thiobis(2-methyl-6-tert-butylphenol). Another product arising by alkylation of thiobisphenol contained only 3.17% of sulphur; its structure was not investigated in more detail.

TABLE I
Properties of Ethers and Partial Ethers of 2,2'- and 4,4'-Alkylidenebisphenols and -Thiobisphenols

Compound	Yield %	M.p., °C (solvent)	Formula (m. w.)	Calculated/Found	
				% C	% H
2-Tert-butyl-4-methyl- -6-(2-methoxy-3-tert-butyl- -5-methylbenzyl)phenol	35.0	141—2 (ethanol)	$C_{24}H_{34}O_2$ (354.5)	81.31 81.18	9.67 9.72
2,2'-Methylenebis(4-methyl- -6-tert-butylanisole)	38.5	glassy melt	$C_{25}H_{36}O_2$ (368.6)	81.47 81.25	9.85 9.85
2-Methyl-6-tert-butyl- -4-(3-methyl-4-methoxy- -5-tert-butylbenzyl)phenol	14.1	101—3 (methanol)	$C_{24}H_{34}O_2$ (354.5)	81.31 81.22	9.67 9.74
4,4'-Methylenebis(2-methyl- -6-tert-butylanisole)	43.5	51—3 (ethanol)	$C_{25}H_{36}O_2$ (368.6)	81.47 81.47	9.85 9.81
2-Tert-butyl-4-methyl- -6-(2-methoxy-3-tert-butyl- -5-methyl- α -propylbenzyl)phenol	75.6	145—6 (ethanol)	$C_{27}H_{40}O_2$ (396.6)	81.77 81.83	10.17 10.26
2,2'-Butylidenebis(4-methyl- -6-tert-butylanisole)	16.1	78—81 (ethanol)	$C_{28}H_{42}O_2$ (410.6)	81.89 81.79	10.30 10.97
2-Methyl-6-tert-butyl- -4-(3-methyl-4-methoxy-5-tert- -butyl- α -propylbenzyl)phenol	19.2	97—99 (hexane)	$C_{27}H_{40}O_2$ (396.6)	81.77 81.83	10.17 10.21
4,4'-Butylidenebis(2-methyl- -6-tert-butylanisole)	47.9	glassy melt	$C_{28}H_{42}O_2$ (410.64)	81.89 81.76	10.30 10.42
2,2'-Benzylidenebis(4-methyl- -6-tert-butylanisole)	86.5	132—4 (hexane)	$C_{31}H_{40}O_2$ (444.6)	83.74 83.85	9.07 8.99
2-Methyl-6-tert-butyl- -4-(3-methyl-4-methoxy-5-tert- -butyl- α -phenylbenzyl)phenol	18.5	125—7 (heptene)	$C_{30}H_{38}O_2$ (430.6)	83.675 83.61	8.89 9.00
4,4'-Benzylidenebis(2-methyl- -6-tert-butylanisole)	47.3	glassy melt	$C_{31}H_{40}O_2$ (444.6)	83.74 83.65	9.07 9.16
2-Tert-butyl-4-methyl- -6-(2-methoxy-3-tert-butyl- -5-methyl- α,α' -dimethylbenzyl)- phenol	87.1	126—7 (ethanol)	$C_{26}H_{38}O_2$ (382.6)	81.77 81.61	10.17 10.13
2-Methyl-6-tert-butyl- -4-(3-methyl-4-methoxy-5-tert- -butyl- α,α' -dimethylbenzyl)phenol	15.1	81—83 (heptane)	$C_{26}H_{38}O_2$ (382.6)	81.77 81.60	10.17 10.17
4,4'-Isopropylidenebis- (2-methyl-6-tert-butylanisole)	50.7	89—91 (methanol)	$C_{27}H_{40}O_2$ (396.6)	81.77 82.10	10.17 10.54

TABLE I
(Continued)

Compound	Yield %	M.p., °C (solvent)	Formula (m.w.)	Calculated/Found	
				% C	% H
2-(2-Methoxy-3-tert-butyl- -5-methylphenylthio)-4-methyl- -6-tert-butylphenol	60.5	80—81.5 (methanol)	C ₂₃ H ₃₂ O ₂ S ^a (372.6)	74.15	8.66
				74.15	8.64
2,2'-Thiobis(4-methyl- -6-tert-butylanisole)	78	105—6 (ethanol)	C ₂₄ H ₃₄ O ₂ S ^b (386.59)	74.56	8.86
				74.37	8.78
4,4'-Thiobis(2-methyl- -6-tert-butylanisole)	80	62—3 (ethanol)	C ₂₄ H ₃₄ O ₂ S ^c (386.59)	74.56	8.86
				74.42	8.82

^{a,b,c} Analysis for S (%; calc./found): ^a 8.61/8.64; ^b 8.29/8.32; ^c 8.29/8.22.

Only 2-tert-butyl-4-methyl-6-(2-methoxy-3-tert-butyl-5-methyl- α,α' -dimethylbenzyl)phenol was obtained from 2,2'-isopropylidenebis(4-methyl-6-tert-butylphenol). The corresponding bisanisole could not be prepared even by repeated alkylation of the partial ether or of its phenoxide by a large excess of dimethyl sulphate. Further etherification is probably prevented by a strong steric hindrance the existence of which was proved already during the investigation of the infrared spectra of the initial 2,2'-isopropylidenebis(4-methyl-6-tert-butylphenol)¹.

EXPERIMENTAL

Chemicals. The starting 2,2'- and 4,4'-alkylidenebisphenols and thiobisphenols were chromatographically pure. Dimethyl sulphate, sodium hydroxide and solvents were chemically pure.

Analytical methods. The structure of the products was determined by elemental analyses and from the analysis of infrared, NMR and mass spectra. TLC was carried out on Silufol UV 254 plates (Kavalier). Ether, benzene, heptane and their mixtures at appropriate ratios were used as eluents.

General alkylation procedure. The starting bisphenol (0.01 mol) was dissolved in ethanol (25 ml), and sodium hydroxide (0.01—0.02 mol powdered) was added to the solution. The mixture was stirred c. 10 min, and dimethyl sulphate (0.02—0.04 mol) was added dropwise with stirring at room temperature for another half hour. The course of the reaction was followed by TLC; after partial ether had been formed in a sufficient concentration or bisphenol had been totally etherified, stirring was interrupted, the reaction mixture neutralized, diluted with water, and extracted with ether. The extract after washing, drying, and concentration was diluted with a small amount of heptane. If any product separated, it was purified by crystallization. The noncrystallizing reaction mixture and mother liquors were separated by column chromatography on silicagel impregnated with dimethylformamide with hexane as the eluent. On washing with water and drying, fractions containing pure products were concentrated and crystallized. The compounds thus obtained are listed in Table I; the yields were calculated in relation to the starting bisphenol.

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