

Antioxidant 2,2'-Selenobis(4-methyl-6-*t*-butylphenol) Preparation, Infrared and Mass Spectra

Š. KORČEK, Š. HOLOTÍK, J. LEŠKO and V. VESELÝ

*Department of Chemistry and Technology of Petroleum,
Slovak Technical University, Bratislava 1*

Received April 20, 1968

In revised form December 10, 1968

2,2'-Selenobis(4-methyl-6-*t*-butylphenol) was prepared by reaction of SeOCl_2 with 2-*t*-butyl-4-methylphenol in anhydrous CHCl_3 . The final product was isolated from the reaction mixture by crystallization and partition chromatography over silica gel using a dimethylformamide-*n*-hexane solvent system; its purity was checked by paper chromatography.

The antioxidant ability of alkyl derivatives of bisphenols with a methylene, sulfidic or disulfidic bridge in *ortho*-(2,2'-bis) or *para*-(4,4'-bis) position to the hydroxyl group is generally known [1]. These compounds were found to be chain breaking inhibitors [2] due to the sterically hindered hydroxyl group; furthermore, they can act as peroxide decomposers which is associated with their sulfur bridge [3, 4]. Bearing in mind the known ability of dialkylselenides to decompose peroxides [5-7] we presumed that alkylated bisphenols with a selenium bridge would also cumulate both above-mentioned properties and consequently, they might be effective antioxidants. That is why we prepared 2,2'-selenobis(4-methyl-6-*t*-butylphenol) the antioxidant properties of which we reported in [8].

The preparation of bisdialkylphenolselenides has as yet not been published and therefore, the synthesis was accomplished in analogy to that of symmetric diarylselenides [9]. A process has been chosen where aromatic hydrocarbons were treated with selenium oxychloride:



This is the only method starting with phenol, cresols and naphthols. Upon treatment with SeOCl_2 , phenol and resorcinol afforded triarylselenonium chlorides $(\text{Ar})_3\text{SeCl}$, whereas *o*- and *p*-cresol led to diarylselenides with selenium in *o*- or *p*-position to hydroxyl group in lower yield. It was assumed that starting from 2-*t*-butyl-4-methylphenol the reaction will be directed by the *t*-butyl group to form even more diarylselenide the type of which is determined by the single free *o*-position.

Experimental

2-*t*-Butyl-4-methylphenol (J. Dimitrov Chemical Works, Bratislava), m.p. 52-53°C (cf. 54.5-55°C in [10]).

Selenium oxychloride was prepared by chlorination of Se and SeO_2 suspended in CCl_4 ; b.p. 174-176°C at 745 torr (cf. 176.4°C at 726 torr [11]).

2,2'-Selenobis(4-methyl-6-*t*-butylphenol). SeOCl_2 (30 g freshly distilled) was diluted with 200 ml CHCl_3 and while stirring, 4-methyl-6-*t*-butylphenol (116 g, mol. ratio

to SeOCl_2 , 3 : 1) in 300 ml anhydrous CHCl_3 was added within 30 minutes. The reaction mixture heated from itself turned dark and hydrogen chloride which has been evolved was removed by boiling after the reaction was through. The reaction mixture thus obtained was analyzed by paper chromatography and purified by partition chromatography.

Paper chromatography was carried out in a solvent system dimethylformamide (50% solution in benzene)—*n*-hexane [12]. It has been assumed that the R_F value of the final product will be high, as hydroxyl groups are shielded by *t*-butyl group in *o*-positions and form, of course, intramolecular hydrogen bonds (see Infrared spectroscopy). This was the reason why all compounds of a high R_F value were isolated from the reaction mixture in a small amount and the final product was characterized by its m.p. and identified by elemental analysis, infrared spectroscopy and mass spectrometry. The R_F value of 2,2'-selenobis(4-methyl-6-*t*-butylphenol) was found to be 0.75.

The reaction mixture consisted of nine components, two of which revealed R_F values close to that of the final product. One of them migrated with the front and disclosed a very weak staining, whereas the second spot of $R_F \approx 0.65$ likewise that of the starting material was very intensive.

There is no difference in behaviour of phenolic substances in the partition chromatography on silica gel or paper if the same solvent system is used. Therefore, silica gel column chromatography could be applied to isolate and purify the wanted final product.

A PHH silica gel (Spolana Neratovice, Works Velvary) with 70% w/w dimethylformamide ($n_D^{20} = 1.4308$; b.p. = 69°C/36.8 torr) as a stationary phase was used to perform the chromatography. *n*-Hexane fractions were analyzed by paper chromatography. Substances of low R_F values were removed first. The *n*-hexane solution of the above-mentioned three compounds was subjected to multiple crystallization. The brown-red substance of $R_F \approx 0.65$ which occurs in mother liquors was found to be an oxidation product of the final product. Crystals containing preponderantly 2,2'-selenobis(4-methyl-6-*t*-butylphenol) were manifold crystallized from ethanol in a carbon dioxide atmosphere.

2,2'-Selenobis(4-methyl-6-*t*-butylphenol) of chromatographic pure grade is a white crystalline substance of m.p. 106–107°C.

For $\text{C}_{22}\text{H}_{30}\text{O}_2\text{Se}$ (405) calculated: 65.17% C, 7.46% H, 19.48% Se; found*: 65.06% C, 7.32% H, 19.90% Se.

Infrared spectroscopy

Infrared spectra of 2,2'-selenobis(4-methyl-6-*t*-butylphenol) were taken with a SP 100 G UNICAM apparatus either in solution (CS_2 , CCl_4 , CHCl_3) or using a KBr technique.** The wavenumber reading was accurate to 1 cm^{-1} .

The comment to the spectrum of 2,2'-selenobis(4-methyl-6-*t*-butylphenol) is given in Table 1. Absorption bands were attributed to single bonds, groups and structures according to spectroscopic data given in [13, 14] and further spectroscopic data reported for alkylphenols [15–18].

* Elemental analysis was carried out in Analytical laboratory of the Department of Analytical Chemistry, Slovak Technical University, Bratislava.

** Infrared spectra were run in the Laboratory of Infrared Spectroscopy, Department of Organic Chemistry, Slovak Technical University, Bratislava.

Table 1

Infrared spectral data of 2,2'-selenobis(4-methyl-6-*t*-butylphenol)

Dissolved			Crystalline	Vibration type	Structure, group, bonding
ν (cm^{-1})	$\Delta\nu_{\frac{1}{2}a}$ (cm^{-1})	ϵ_a ($\text{l mol}^{-1} \text{cm}^{-1}$)	ν (cm^{-1})		
758	12	110	759		
780	7	135	777		
865	12	130	866	$\gamma(\text{C—H})$	
938	10	50	938		
1032	—	35	—		
1100	14	50	1100		
1180	15	390	1182	$\nu(\text{C—O})?$	$\text{C}_6\text{H}_5\text{—OH}?$
1205	13	205	1205	ν_3 skeletal?	$\text{—C—}(\text{CH}_3)_3?$
1223	—	(100)	1220		
1242	11	360	1242	ν_2 skeletal?	$\text{—C—}(\text{CH}_3)_3?$
1281	12	165	1281		
1333	17	185	1338	$\delta(\text{O—H} \dots \text{X})?$	$\text{C}_6\text{H}_5\text{—OH}?$
—	—	—	1359		
1366	11	170	1366	$\delta_s(\text{C—H})$	$\text{—C—}(\text{CH}_3)_3$
1395	(12)	(170)	1396		
1445	14	510	1442	$\delta_{as}(\text{C—H})$	—CH_3
1471	—	—	(1466)		
1488	—	—	1486	in-plane C=C skeletal vibrations	aromatic nuclei forming a conjugated system
1582	20	30	1577		
1605	—	—	(1601)		
(1714)	—	5	—	$\gamma(\text{C—H})$	grouping characteristic for the 1, 2, 3, 5 substitution of the nucleus
1756	22	15	(1758)		
1792	(18)	5	—		
2867	—	(140)	—		
2911	—	(220)	—	$\nu(\text{C—H})$	—CH_3
2956	35	370	—		
2997	—	(105)	—	$\nu(\text{C—H})?$	aromatic ring
3424	(50)	150	3404		
3495	—	(80)	—	$\nu(\text{O—H})$	}intramolecular —O—H (free)
3629	—	20	—		

Note: Approximate values are in brackets.

Hydroxyl groups in solutions are either free (band at 3629 cm^{-1}) or form intramolecular hydrogen bonds (bands at 3424 and 3495 cm^{-1}). Hydroxyl group in a crystalline state forms exclusively intramolecular hydrogen bond of one kind (band at 3404 cm^{-1}).

Taken in conjunction with a paper by *Binder, Ambelang and Webb* [19] who studied an analogous thio compound and with that by *David and Hallam* [20] who examined hydrogen bonds $\text{—O—H} \dots \text{S}$ in *o*-hydroxythiophenols it would be possible to attribute the band at 3424 (3404) cm^{-1} to $\text{—O—H} \dots \text{Se}$ grouping, which might exist in the *trans* configuration of the prepared substance; band at 3495 cm^{-1} might be associated with the $\text{—O—H} \dots \text{O}$ grouping between two hydroxyls in the *cis* configuration. According to the recent paper by *Cairns and Eglinton* [21] the band at 3424 cm^{-1} should be due

to the $-O-H \dots O$ grouping whereas that at 3495 cm^{-1} is subject to $-O-H \dots \pi$ bond between hydroxyl group and π electrons of the neighbouring benzene ring. To establish the type of the hydrogen bond just on the basis of bands occurring at 3424 (3404) cm^{-1} and 3495 cm^{-1} requires further study.

Mass spectrometry

Mass spectrum was recorded with a MCh 1306 mass spectrometer (U. S. S. R.) at 70 eV (ionizing electrons energy) and 150°C (ionization chamber temperature) [22].

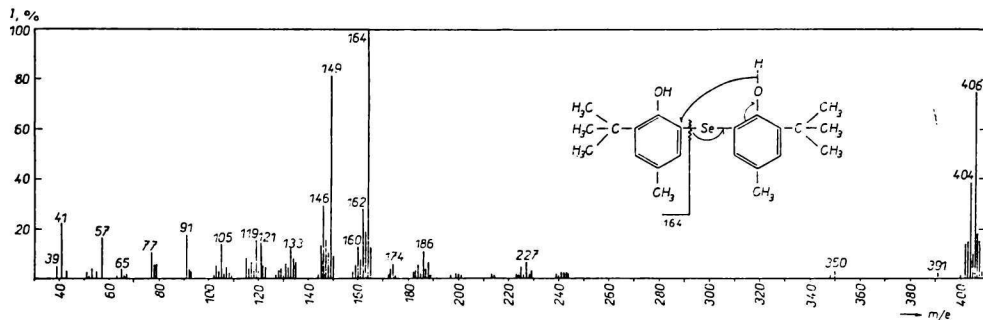
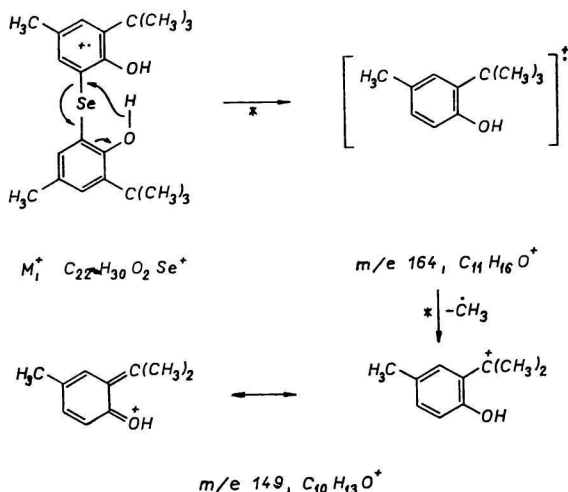
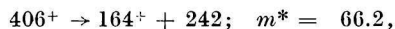


Fig. 1. Mass spectrum of 2,2'-selenobis(4-methyl-6-*t*-butylphenol).

The mass spectrum of 2,2'-selenobis(4-methyl-6-*t*-butylphenol) (Fig. 1) is at the first sight characterized by distribution of the molecular ions $\text{C}_{22}\text{H}_{30}\text{O}_2\text{Se}^+$ intensities, due to six selenium isotopes [23]. The parent peak in the spectrum is a m/e 164 species (Fig. 1); its formation and decomposition can be illustrated in Chart 1.



This fragmentation is supported by metastables peaks at m/e 66.2 and 135.3



The relative intensity of the remaining peaks is less than 30%. The peaks resulted either from a simple fission of bonds or from decomposition and hydrogen transfers.

References

1. Kalichevsky V. A., Kobe K. A., *Petroleum Refining with Chemicals*. Elsevier, Amsterdam, 1956.
2. Korček Š., Baxa J., Veselý V., *Collect. Czech. Chem. Commun.* **33**, 2458 (1968).
3. Baková B., *Thesis*. Slovak Technical University, Bratislava, 1963.
4. Pieš R., *Thesis*. Slovak Technical University, Bratislava, 1964.
5. Denison G. H., Condit P. C., *U. S. Patent* 2 398 415 (1946); *U. S. Patent* 2 473 510 (1949).
6. Heiks R. E., Croxton F. C., *Ind. Eng. Chem.* **39**, 1466 (1947).
7. Denison G. H., Condit P. C., *Ind. Eng. Chem.* **41**, 944 (1949).
8. Korček Š., Baxa J., Veselý V., *Collect. Czech. Chem. Commun.*, in press.
9. Houben, Weyl, *Methoden der organischen Chemie*, Band IX, pp. 987–994, 1006, 1018. Georg Thieme Verlag, Stuttgart, 1955.
10. Stroh R., Seydel R., Hahn W., *Angew. Chem.* **69**, 699 (1957).
11. Lenher V., *J. Amer. Chem. Soc.* **42**, 2498 (1920).
12. Korček Š., Baxa J., Veselý V., *Chem. Zvesti* **23**, 301 (1969).
13. Bellamy L. J., *Infrakrasnyje spektry složnych molekul. (The Infrared Spectra of Complex Molecules.)* Izdatelstvo inostrannoj literatury, Moscow, 1963.
14. Nakanishi K., *Infrakrasnyje spektry i strojenije organičeskich sojedinenij. (Infrared Absorption Spectroscopy.)* Izdatelstvo Mir, Moscow, 1965.
15. Favre J., Parc G., *Rev. Inst. Fr. Petrole Ann. Combust. Liquides* **13**, 267 (1958).
16. Ingold K. U., *Can. J. Chem.* **38**, 1092 (1960).
17. Ingold K. U., Taylor D. R., *Can. J. Chem.* **39**, 461 (1961).
18. Parc H., *Rev. Inst. Fr. Petrole Ann. Combust. Liquides* **15**, 567, 680 (1960).
19. Binder J. L., Ambelang J. C., Webb F. J., *J. Amer. Chem. Soc.* **81**, 3608 (1959).
20. David J. G., Hallam H. E., *Spectrochim. Acta* **21**, 841 (1965).
21. Cairns T., Eglinton G., *J. Chem. Soc.* **1965**, 5906.
22. Kováčik V., *CSc. Thesis*. Institute of Chemistry, Slovak Academy of Sciences, Bratislava, 1967.
23. Beynon J. H., *Mass Spectrometry and Its Applications to Organic Chemistry*, p. 558. Elsevier, Amsterdam, 1960.

Translated by Z. Votický