PIPERAZINOPHENOLS AS STABILIZERS FOR UNSATURATED COMPOUNDS AND THEIR CHLORO DERIVATIVES

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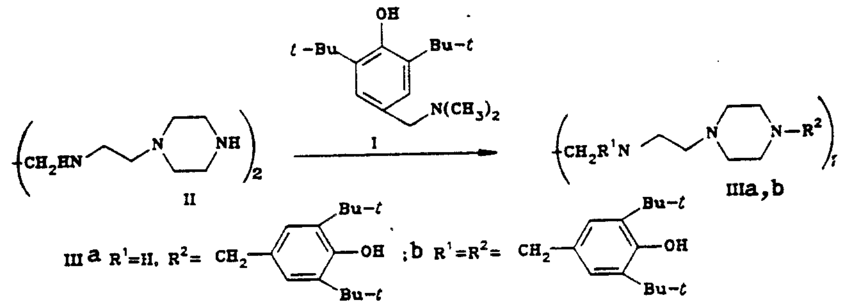
Polyfunctional piperazinophenols, which are effective stabilizers during the distillation or storage of unsaturated hydrocarbons and their chloro derivatives, were obtained by the aminomethylation of phenols, which proceeds with the participation of piperazine and N,N'-bis(piperazinoethyl)ethylenediamine.

Dialkylphenol derivatives are used as antioxidants for colorless polymers [1]. The easily realized reaction of cyclic polyamines with Mannich base I makes it possible to obtain unknown derivatives that are of interest as stabilizers for polymers, antioxidants, and inhibitors for unsaturated compounds and their chloro derivatives [2-4]. The compounds such as alkyldiethylenetriamines that have been proposed as stabilizers for halogenated hydrocarbons [5, 6] have little effect and are slightly soluble in organochlorine products.

Piperidine readily undergoes condensation with N,N-dimethyl-3,5-di-tert-butyl-4-hydroxybenzylamine (I) to give N-(3,5-di-tert-butyl-4-hydroxybenzyl)piperazine in 60% yield [2]. N,N'-Bis(piperazinoethyl)ethylenediamine (II) (a new derivative of ethylenediamine) was obtained by the reaction of N-(β-aminoethyl)piperazine with dichloroethane. The PMR spectrum of II contains a signal at 1.72 ppm, the area of which corresponds to four NH protons. The signal at 2.47 ppm corresponds to ten methylene groups, eight of which enter into the piperazine ring, while two are linked with tertiary nitrogen atoms. The multiplet centered at 2.74 ppm is related to four methylene groups bonded to an ethylenediamine fragment. Compound II also reacts readily with Mannich base I to give, depending on the reagent ratio, both di- and tetrahydroxybenzyl derivatives IIIa, b.



The IR spectra of IIIa, b contain a narrow absorption band at 3570 cm^{-1}, which is characteristic for the hydroxy group of shielded phenols.

Piperazines also react readily with bisphenols; depending on the reagent ratio, the corresponding mono- or disubstituted derivatives IVa-d are formed. The reaction of bisphenols with piperazines takes place at moderate temperatures in low-boiling alcohols as the media (Table 1).

The IR spectrum of IVc does not contain the absorption band at 1570 cm^{-1} that is characteristic for the NH group (see scheme below).

Compounds IIIa, b and N-(3,5-di-tert-butyl-4-hydroxybenzyl)piperazine were tested as stabilizers for unsaturated hydrocarbons and their chloro derivatives [2, 3]. As one can see from [2, 3], piperazinophenols decrease the percentage of resinification of unsaturated hydrocarbons and their chloro derivatives and, with respect to their action, surpass known stabilizers [5, 6].

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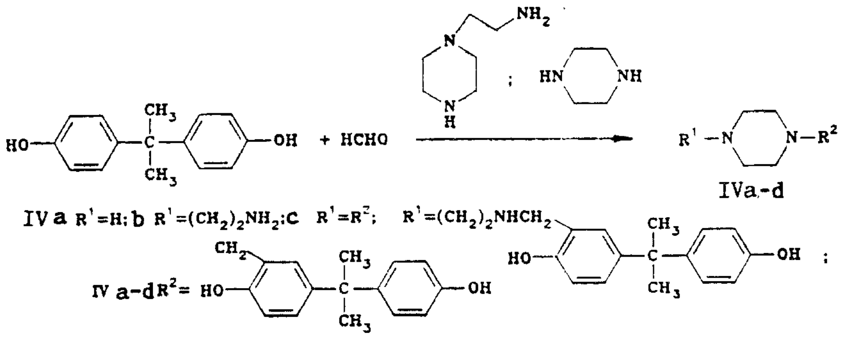

EXPERIMENTAL

The IR spectra of thin layers or suspensions of the compounds in Nujol were recorded with a UR-20 spectrometer. The PMR spectra of solutions in CCl_4 were obtained with a Tesla BS-487 spectrometer (80 MHz) with hexamethyldisiloxane (HMDS) as the internal standard. Analysis of the piperazines by GLC was carried out with an LKhM-7A chromatograph with a catharometer at 175°C; the column was 5 m long and packed with Ftoroplast-4, and the stationary phase was E 301 silicone elastomer.

The results of elementary analysis of the synthesized II-IV were in agreement with the calculated values.

N-(β-Aminoethyl)piperazine. This compound was isolated by precise rectification of the mixture of polyethylenepolyamines – the side products in the manufacture of ethylenediamine. According to GLC data, the percentage of the product was 99.5%, with bp 127°C, n_D^{20} 1.4998, and d_4^{20} 0.9842 g/cm³.

N,N'-Bis(piperazinoethyl)ethylenediamine (II). A solution of 25.8 g of N-(β-aminoethyl)piperazine and 9.9 g of dichloroethane in 50 ml of methanol was refluxed for 8 h, after which 11.2 g of KOH was added with stirring. The precipitated potassium chloride was removed by filtration, the methanol was evaporated, and the product was distilled in vacuo.

N,N'-Bis{N-[4-hydroxy-3,5-di-tert-butylbenzyl]piperazinoethyl}ethylenediamine (IIIa). A 52.6 g sample of Mannich base I in 100 ml of isopropyl alcohol was added to a heated (to 80°C) solution of 35.7 g of the dihydrochloride of II in 25 ml of isopropyl alcohol, after which the reaction mixture was heated for 6 h at 85-90°C, with simultaneous removal of the alcohol by distillation. The product was purified by crystallization from diethyl ether–petroleum ether (1:2).

1,2,3,4-Tetrakis(4-hydroxy-3,5-di-tert-butylbenzyl)-N,N'-bis(piperazinomethyl)ethylenediamine (IIIb). A mixture of 14.2 g of II and 52.6 of Mannich base I in 100 ml of methanol was heated for 10 h at 70°C. Product IIIb was purified by recrystallization from diethyl ether–petroleum ether (1:1).

2-(4-Hydroxybenzyl)-2-(3-piperazinomethyl-4-hydroxyphenyl)propane (IVa). A mixture of 8.6 g of piperazine, 22.8 g of diphenylolpropane, and 10 ml of 36% aqueous formaldehyde was heated for 6 h at 50°C. The product was purified from alcohol–ether (1:3).

2-(4-Hydroxyphenyl)-2-(3-ethylaminopiperazinomethyl-4-hydroxyphenyl)propane (IVb). A mixture of 12.9 g of N-(β-aminoethyl)piperazine, 10 ml of 36% aqueous formaldehyde, and 22.8 g of diphenylpropane was heated for 6 h at 85°C. The product was isolated by crystallization from alcohol–ether (1:2). IR spectrum: 1650 cm⁻¹ (NH).

TABLE 1. Characteristics of II-IV

Compound*	Empirical formula	mp, °C	IR spectrum, cm⁻¹	Yield, %
II	$C_{14}H_{32}N_6$	—**	1570 (NH)	95
IIIa	$C_{44}H_{78}Cl_2N_6O_2$	260...262	3570 (OH)	63
IIIb	$C_{74}H_{120}N_6O_4$	157...159	3570 (OH)	50
IVa	$C_{20}H_{26}N_2O_2$	262...263	1565 (NH)	64
IVb	$C_{22}H_{32}N_3O_2$	108...110	1650 (NH)	65
IVc	$C_{36}H_{42}N_2O_4$	125	—	76
IVd	$C_{38}H_{47}N_3O_4$	193...195	1570 (NH)	72

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*Compound II was recrystallized from ether.

**This compound had bp 258-260°C (10 mm).

N,N'-Bis[2,2-di(4-hydroxyphenyl)propane]piperazine (IVc). An 8.6 g sample of piperazine and 45.6 g of diphenylolpropane in 75 ml of methanol and 40 ml of 36% aqueous formaldehyde was heated for 4 h at 70°C. The product was purified by crystallization from ether.

N,N'-Bis[2,2-di(4-hydroxyphenyl)propane]-N-(β-aminoethyl)piperazine (IVd). A mixture of 12.9 g of N-(β-aminoethyl)piperazine, 25 ml of 36% aqueous formaldehyde, and 45.6 g of diphenylpropane was heated for 10 h, initially at 40°C, and then at 90°C. The product was purified by crystallization from alcohol–ether (1:2).

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SYNTHESIS OF FLUORO-SUBSTITUTED SYMMETRICAL DIALKYLAMINOTRIAZINES UNDER INTERPHASE-CATALYSIS CONDITIONS

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The reaction of chloro derivatives of symmetrical dialkylaminotriazines with potassium fluoride in the presence of catalytic amounts of crown ethers or quaternary ammonium salts leads to the formation of the corresponding fluoro derivatives in high yields. The structure of the catalyst and the nucleophilicity of the solvent affect the yields of the fluoro derivatives of the symmetrical dialkylaminotriazines.

Fluoro-substituted symmetrical dialkylaminotriazines are promising intermediates in the synthesis of biologically active compounds and, therefore, their production is an important and urgent task.

Due to the decreased π-electron density on the carbon atoms of the heteroring, symmetrical dialkylaminotriazine are active in nucleophilic substitution reaction, the ease of which decreases with the degree to which electron-donor substituents are introduced into the triazine molecule. The reactivities of the compounds decrease in the following order: trichloro-, dichloro-, and monochlorotriazines [1].

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