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## ORGANIC SYNTHESIS AND INDUSTRIAL ORGANIC CHEMISTRY

# Synthesis and Antioxidative Activity of *N*,*N*-Dialkyl-ω-[4-hydroxy(methoxy)aryl]alkylamines and Their *N*-Oxides

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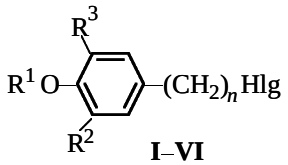
**Abstract**—Aminoalkylphenols of various structures were prepared by reactions of ω-[4-hydroxy(methoxy)-aryl]haloalkanes with dialkylamines. The corresponding *N*-oxides were prepared by oxidation of aminoalkylphenols with hydrogen peroxide and cumene hydroperoxide. The inhibiting activities of these compounds in a model reaction of thermal autooxidation of lard were compared.

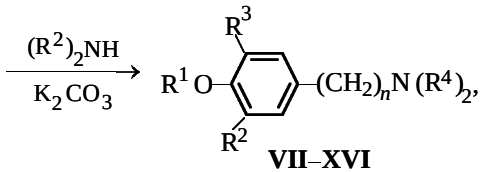
Aminoalkylphenols containing a phenolic fragment and an alkylamino group are highly effective inhibitors of free-radical oxidation of various organic substrates. According to patent data [1–3], they can be used as stabilizers of polymeric materials, rubbers, lubricating oils, and diesel and jet fuels. Furthermore, aminoalkylphenols show a wide spectrum of biological activity; in particular, they exhibit antiphlogistic, antirheumatic, antiallergic, antidiabetic, and other properties [4–10]. The mechanism of the antioxidative effect of aminoalkylphenols responsible for their high performance is not yet fully elucidated; for its better understanding, it is necessary to study the structure–inhibiting activity relationship for aminoalkylphenols and to examine their oxidation products in which one of the groups responsible for the antioxidative power is inactivated.

Therefore, in this study we prepared aminoalkylphenols differing in the extent of steric shielding of the phenolic OH group, structure of the *N*-substituents, and distance between the amino group and aromatic core; also we prepared the corresponding *N*-oxides and compared the inhibiting powers of the compounds synthesized in the model reaction of thermal autooxidation of lard.

By the reaction of ω-[4-hydroxy(methoxy)aryl]-haloalkanes **I**–**VI** with dialkylamines, we prepared the corresponding alkylphenols **VII**–**XVI**:



**I**–**VI**



**VII**–**XVI**

where $R^1$ = H, $R^2$ = $R^3$ = *t*-Bu: *n* = 2, Hlg = Cl (**I**); *n* = 2, $R^4$ = Me (**VII**), Et (**VIII**); *n* = 3, Hlg = Cl (**II**); *n* = 3, $R^4$ = Me (**IX**), Et (**X**), Pr (**XI**); *n* = 4, Hlg = Cl (**III**); *n* = 4, $R^4$ = Me (**XII**), Et (**XIII**); $R^1$ = $R^2$ = H, $R^3$ = *t*-Bu, *n* = 3: Hlg = Cl (**IV**), $R^4$ = Me (**XIV**); $R^1$ = $R^2$ = $R^3$ = H, *n* = 3: Hlg = Br (**V**), $R^4$ = Me (**XV**); $R^1$ = Me, $R^2$ = $R^3$ = H, *n* = 3: Hlg = Br (**VI**), $R^4$ = Me (**XVI**).

The syntheses were performed in ampules in ethanol in the presence of $K_2CO_3$ at 120°C for 7 h; the molar ratio of the starting haloalkane, dialkylamine, and $K_2CO_3$ was 1 : 2 : 2. Yields of **VII**–**XVI** 60–93%.

It is known [11–14] that tertiary aliphatic amines react with peroxy compounds to form *N*-oxides. We performed the oxidation of aminoalkylphenols **IX**–**XI** with hydrogen peroxide and cumene hydroperoxide in 2-propanol at 60°C for 3 h and obtained the corre-

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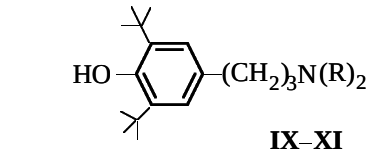
Induction period τ of lard oxidation, inhibited by phenolic antioxidants (1.5 μmol $g^{-1}$, 130°C)

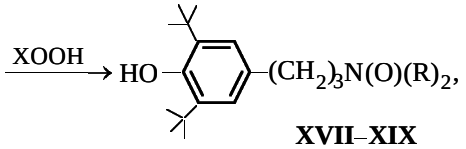
| Antioxidant* | τ, min |
|---|---|
| $R(CH_2)_2N(Me)_2$ (**VII**) | 288 ± 10 |
| $R(CH_2)_2N(Et)_2$ (**VIII**) | 298 ± 7 |
| $R(CH_2)_3N(Me)_2$ (**IX**) | 334 ± 5 |
| $R(CH_2)_3N(Et)_2$ (**X**) | 307 ± 5 |
| $R(CH_2)_3N(Pr)_2$ (**XI**) | 277 ± 7 |
| $R(CH_2)_4N(Me)_2$ (**XII**) | 435 ± 5 |
| $R(CH_2)_4N(Et)_2$ (**XIII**) | 335 ± 5 |
| $R'(CH_2)_3N(Me)_2$ (**XIV**) | 143 ± 5 |
| $R''(CH_2)_3N(Me)_2$ (**XV**) | 51 ± 5 |
| $R(CH_2)_3N(O)(Me)_2$ (**XVII**) | 170 ± 5 |
| $R(CH_2)_3N(O)(Et)_2$ (**XVIII**) | 150 ± 5 |
| $R(CH_2)_3N(O)(Pr)_2$ (**XIX**) | 110 ± 5 |
| $RCH_2N(Me)_2$ (**XX**) | 110 ± 5 |
| $RCH_3$ (Ionol) | 165 ± 5 |
| $C_{12}H_{25}N(Me)_2$ (DMDA) | 20 ± 3 |
| $RCH_3$ + DMDA (synergistic mixture) | 198 ± 5 |
| Control | 20 ± 3 |

* R = 3,5-di-*tert*-butyl-4-hydroxyphenyl, R' = 3-*tert*-butyl-4-hydroxyphenyl, and R'' = 4-hydroxyphenyl.

sponding *N*-oxides **XVII**–**XIX** in 43–90% yields:



**IX**–**XI**



**XVII**–**XIX**

where X = H, $PhC(Me)_2$; R = Me (**XVII**), Et (**XVIII**), Pr (**XIX**).

The compositions and structures of aminoalkylphenols **VII**–**XVI** and their *N*-oxides **XVII**–**XIX** were confirmed by elemental analysis and spectroscopy. In the $^1H$ NMR spectra of *N*-oxides **XVII**–**XIX**, compared to the corresponding aminoalkylphenols **IX**–**XI**, the signals of the methylene protons of the *p*-alkyl substituent are shifted downfield, which suggests an increase in the polarizing power of the N-containing fragment, i.e., its oxidation. The IR spectra of **XVII**–**XIX** contain absorption bands at 950–970 $cm^{-1}$, characteristic of the N–O stretching vibrations. These bands are absent in the spectra of the corresponding aminoalkylphenols **IX**–**XI**.

A search in the STN International database showed that compounds **VIII**, **XI**–**XIV**, and **XVII**–**XIX** were unknown previously. Aminoalkylphenol **VII** is mentioned in [6] without spectral characteristics, and amines **XV** and **XVI** are reported in [8] only as hydrochlorides.

The antioxidative activity (AOA) of aminoalkylphenols **VII**–**XV** and their *N*-oxides **XVII**–**XIX** was evaluated from their inhibiting effect on thermal autooxidation of lard. As references we used commercial inhibitors 2,6-di-*tert*-butyl-4-methylphenol (Ionol) and *N*,*N*-dimethyl(3,5-di-*tert*-butyl-4-hydroxybenzyl)amine **XX**, and also a 1 : 1 synergistic mixture of Ionol and *N*,*N*-dimethyldodecylamine (DMDA).

We found that di-*tert*-butyl-substituted aminoalkylphenols **VII**–**XIII** are effective inhibitors of lard oxidation (see table); in their antioxidative power they appreciably surpass the commercial antioxidants and the Ionol–DMDA mixture.

A previous study of the antiradical activity of 2,6-di-*tert*-butyl-substituted aminoalkylphenols **VII**, **IX**, and **XX** in a model reaction of initiated oxidation of methyl oleate in chlorobenzene at 60°C showed that these compounds are highly reactive toward peroxy radicals [15]. The rate constants $k_7$ of their reaction with peroxy radicals

$$PhOH + ROO^{\bullet} \longrightarrow PhO^{\bullet} + ROOH \qquad (1)$$

were similar to those characteristic of Ionol. This fact suggests that the higher inhibiting power of aminoalkylphenols **VII**–**XIII**, compared to Ionol, in autooxidation of lard is due to the bifunctional mechanism of theit antioxidative effect, namely, to a combination of the antiradical activity of the phenolic group and antioxidative activity of the alkylamino group. The significance of the contribution of the alkylamino group to AOA of aminoalkylphenols is also confirmed by the fact that the corresponding *N*-oxides **XVII**–**XIX** are comparable with, or even inferior to Ionol as inhibitors of lard oxidation. The low AOA of benzylamino derivative **XX** compared to aminoalkylphenols **VII**–**XIII** in oxidation of lard at 130°C is apparently caused by the thermal instability of **XX** [16].

It is known [17, 18] that aliphatic amines in mixtures with phenolic antioxidants can act as synergistic agents. The synergistic effect is usually evaluated by the induction period and characterized by $\Delta\tau_{syn}$ [19]:

$$\Delta\tau_{syn} = \tau_{1,2} - (\tau_1 + \tau_2),$$

where $\tau_{1,2}$ is the induction period in the presence of two inhibitors; $\tau_1$ and $\tau_2$, induction periods in the presence of individual inhibitors.

In the experiments on lard oxidation, the nonadditive effect of coinhibitors was revealed for the system Ionol–DMDA; the synergistic effect, calculated by the formula

$$\Delta\tau_{syn} = (\tau_{PhOH+DMDA} - \tau_0) - (\tau_{DMDA} + \tau_{PhOH} - 2\tau_0),$$

where $\tau_0$ is the induction period of the noninhibited oxidation of lard; $\tau_{DMDA}$ and $\tau_{PhOH}$, induction periods in the presence of DMDA and Ionol, respectively; and $\tau_{PhOH+DMDA}$, induction period in the presence of the Ionol–DMDA mixture, amounted to 33 min. For 2,6-di-*tert*-butyl-substituted aminoalkylphenols **VII**–**XIII**, the synergistic effect was more pronounced, and $\Delta\tau_{syn}$, calculated as

$$\Delta\tau_{syn} = (\tau_{AAP} - \tau_0) - (\tau_{DMDA} + \tau_{PhOH} - 2\tau_0),$$

where $\tau_{AAP}$ is the induction period of lard oxidation in the presence of aminoalkylphenols, ranged from 112 to 270 min. Thus, we can state that the high antioxidative acitivity of aminoalkylphenols in lard oxidation is associated not only with the bifunctional mechanism of their antioxidative effect but also with the pronounced synergistic effect which, most likely, is of intramolecular origin and is due to structural features of these molecules.

The occurrence of intramolecular synergism in bifunctional inhibitors, in particular, in sulfur-containing derivatives of sterically hindered phenols, was repeatedly discussed in [20–22]; however, its origin was not elucidated. The intramolecular synergism may be due to favorable steric arrangement of the phenolic and sulfur-containing fragments, allowing the hydroperoxide formed by reaction (1) to be deactivated with the sulfur-containing fragment without escaping into the bulk of the substrate [22]. A similar pattern can be expected for aminoalkylphenols.

Since the extent of the intramolecular synergism can depend on the distance between the alkylamino group and aromatic core, the difference in the AOA of aminoalkylphenols **VII**–**X**, **XII**, **XIII**, and **XX** containing different number of carbon atoms in the *p*-alkyl chain becomes quite understandable. In the series of *N,N*-dimethyl- and diethyl-substituted aminoalkylphenols, in the most effective inhibitors of lard oxidation the alkylamino group was separated from the aromatic core by four carbon atoms. Apparently, in this case the mutual arrangement of the phenolic and alkylamino groups is the most favorable for the intramolecular synergism.

The antioxidative activity of aminoalkylphenols also strongly depended on the structure of *N*-substituents and extent of steric shielding of the phenolic OH group. In going from *N,N*-dimethyl-substituted amine **IX** to its diethyl (**X**) and dipropyl (**XI**) analogs, the inhibiting activity decreased.

Aminoalkylphenols differing in the extent of steric shielding of the phenolic OH group can be ranked in the following order with respect to the capability to inhibit lard oxidation: **IX** > **XIV** > **XV**. A decrease in AOA of aminoalkylphenols in this series corresponds to an increase in the reactivity of the corresponding phenoxy radicals in the reaction

$$PhO^{\bullet} + RH \longrightarrow PhOH + R^{\bullet}. \qquad (2)$$

In particular, according to the existing estimates, *o*-unsubstituted phenoxyls are $10^3$–$10^4$ times (at 60°C) more active than 2,6-di-*tert*-butyl-substituted phenoxy radicals [23]. Compound **XV** at the *o*-positions contains no bulky *tert*-butyl substituents sterically hindering reaction (2), which accounts for the lowest AOA of this compound in the examined series.

## EXPERIMENTAL

The $^1$H NMR spectra were recorded on a Bruker spectrometer (500 MHz), solvents $CDCl_3$ and $CD_3OD$, internal reference TMS; the IR spectra were taken on a Specord M80 spectrometer in $CHCl_3$. The melting points were determined on a PTP device. The starting ω-[4-hydroxy(methoxy)aryl]haloalkanes **I**–**VI** were prepared as described previously [24], and *N,N*-dimethyl(3,5-di-*tert*-butyl-4-hydroxybenzyl)amine **XX**, by the procedure described in [3].

***N,N*-Dimethyl-2-(3,5-di-*tert*-butyl-4-hydroxyphenyl)ethylamine VII.** A 50-ml ampule was charged with 5.0 g (18.6 mmol) of chloride **I**, 5.1 g of dimethylamine solution (37.2 mmol), 5.1 g (37.2 mmol) of $K_2CO_3$, and 10 ml of ethanol. The ampule was sealed, placed in a thermostat equipped with a shaker, and heated for 7 h at 120°C. After cooling, the ampule was opened, and the reaction mixture was treated with alkali and extracted with toluene. The extract was washed with water and dried over $Na_2SO_4$; the solvent was distilled off, and the residue was distilled in a vacuum. Yield of amine **VII** 4.0 g (78%), bp 140–142°C (1 mm Hg), mp 84–85°C. $^1$H NMR spectrum, δ, ppm: 1.44 s (18H, *t*-Bu), 2.32 s [6H, $N(CH_3)_2$], 2.55 m (2H, $CH_2N$), 2.69 m (2H, $ArCH_2$), 4.91 s (1H, OH), 6.99 s (2H, $H_{arom}$). IR spectrum, ν, cm$^{-1}$: 3640 (OH).

Found, %: C 78.08, H 11.47, N 5.39.
$C_{18}H_{31}ON$.
Calculated, %: C 77.92, H 11.26, N 5.05.

***N*,*N*-Diethyl-2-(3,5-di-*tert*-butyl-4-hydroxyphenyl)ethylamine VIII** was prepared similarly from 5.2 g (19.3 mmol) of chloride **I**, 2.8 g (38.7 mmol) of diethylamine, and 5.4 g (38.7 mmol) of $K_2CO_3$. Yield 5.4 g (91%), bp 122–124°C (1 mm Hg). $^1$H NMR spectrum, δ, ppm: 1.08 t [6H, $N(CH_2CH_3)_2$], 1.45 s (18H, *t*-Bu), 2.63 q [4H, $N(CH_2CH_3)_2$], 2.69 s (4H, $ArCH_2CH_2$), 5.07 s (1H, OH), 7.01 s (2H, $H_{arom}$). IR spectrum, ν, cm$^{-1}$: 3640 (OH).

Found, %: C 78.48, H 11.47, N 4.24.
$C_{20}H_{35}ON$.
Calculated, %: C 78.63, H 11.55, N 4.58.

***N*,*N*-Dimethyl-3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propylamine IX** was prepared similarly from 5.0 g (17.7 mmol) of chloride **II**, 4.8 g of dimethylamine solution (35.4 mmol), and 4.9 g (35.4 mmol) of $K_2CO_3$. Yield 4.6 g (90%), bp 130°C (1 mm Hg), mp 44–45°C (published data: 31–33°C) [5]. $^1$H NMR spectrum, δ, ppm: 1.49 s (18H, *t*-Bu), 1.82 m (2H, $ArCH_2CH_2$), 2.30 s [6H, $N(CH_3)_2$], 2.38 t (2H, $CH_2N$), 2.60 t (2H, $ArCH_2$), 5.11 s (1H, OH), 7.06 s (2H, $H_{arom}$). IR spectrum, ν, cm$^{-1}$: 3640 (OH).

Found, %: C 78.11, H 11.58, N 4.81.
$C_{19}H_{33}ON$.
Calculated, %: C 78.29, H 11.41, N 4.85.

***N*,*N*-Diethyl-3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propylamine X** was prepared similarly from 4.7 g (16.7 mmol) of chloride **II**, 2.4 g (33.4 mmol) of diethylamine, and 4.6 g (33.4 mmol) of $K_2CO_3$. Yield 4.9 g (93%), bp 150–153°C (1 mm Hg). $^1$H NMR spectrum, δ, ppm: 1.04 t [6H, $N(CH_2CH_3)_2$], 1.46 s (18H, *t*-Bu), 1.79 m (2H, $ArCH_2CH_2$), 2.50–2.58 m [8H, $ArCH_2$, $CH_2N$, $N(CH_2CH_3)_2$], 5.05 s (1H, OH), 7.02 s (2H, $H_{arom}$). IR spectrum, ν, cm$^{-1}$: 3640 (OH).

Found, %: C 78.82, H 11.75, N 4.22.
$C_{21}H_{37}ON$.
Calculated, %: C 78.94, H 11.67, N 4.38.

***N*,*N*-Dipropyl-3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propylamine XI** was prepared similarly from 5.0 g (17.5 mmol) of chloride **II**, 3.8 g (35.1 mmol) of dipropylamine, and 4.8 g (35.1 mmol) of $K_2CO_3$. Yield 5.1 g (84%), bp 161–164°C (2 mm Hg). $^1$H NMR spectrum, δ, ppm: 0.96 t [6H, $N(CH_2CH_2 \cdot CH_3)_2$], 1.51 s (18H, *t*-Bu), 1.51 m [4H, $N(CH_2 \cdot CH_2CH_3)_2$], 1.77 m (2H, $ArCH_2CH_2$), 2.43 t [4H, $N(CH_2CH_2CH_3)_2$], 2.48 t (2H, $CH_2N$), 2.58 t (2H, $ArCH_2$), 4.96 s (1H, OH), 6.97 s (2H, $H_{arom}$). IR spectrum, ν, cm$^{-1}$: 3640 (OH).

Found, %: C 79.89, H 11.95, N 4.05.
$C_{23}H_{41}ON$.
Calculated, %: C 79.49, H 11.89, N 4.03.

***N*,*N*-Dimethyl-4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)butylamine XII** was prepared similarly from 5.0 g (16.8 mmol) of **III**, 4.6 g of dimethylamine solution (33.7 mmol), and 4.7 g (33.7 mmol) of $K_2CO_3$. Yield 4.4 g (85%), bp 148–150°C (1 mm Hg), mp 90–91°C. $^1$H NMR spectrum, δ, ppm: 1.47 s (18H, *t*-Bu), 1.57 m (2H, $ArCH_2CH_2CH_2$), 1.63 m (2H, $ArCH_2CH_2$), 2.26 s [6H, $N(CH_3)_2$], 2.32 t (2H, $CH_2N$), 2.58 t (2H, $ArCH_2$), 5.07 s (1H, OH), 7.01 s (2H, $H_{arom}$). IR spectrum, ν, cm$^{-1}$: 3640 (OH).

Found, %: C 78.97, H 11.81, N 4.65.
$C_{20}H_{35}ON$.
Calculated, %: C 78.63, H 11.55, N 4.58.

***N*,*N*-Diethyl-4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)butylamine XIII** was prepared similarly from 5.2 g (17.5 mmol) of **III**, 2.6 g (35.0 mmol) of diethylamine, and 4.8 g (35.0 mmol) of $K_2CO_3$. Yield 5.3 g (91%), bp 145–147°C (1 mm Hg). $^1$H NMR spectrum, δ, ppm: 1.06 t [6H, $N(CH_2CH_3)_2$], 1.48 s (18H, *t*-Bu), 1.60 m (4H, $ArCH_2CH_2CH_2$), 2.49–2.58 m [8H, $N(CH_2CH_3)_2$, $CH_2N$, $ArCH_2$], 5.05 s (1H, OH), 7.02 s (2H, $H_{arom}$). IR spectrum, ν, cm$^{-1}$: 3640 (OH).

Found, %: C 79.65, H 11.81, N 4.05.
$C_{22}H_{39}ON$.
Calculated, %: C 79.92, H 11.78, N 4.20.

***N*,*N*-Dimethyl-3-(3-*tert*-butyl-4-hydroxyphenyl)propylamine XIV** was prepared similarly from 5.0 g (22.1 mmol) of chloride **IV**, 6.0 g of dimethylamine solution (44.1 mmol), and 6.1 g (44.1 mmol) of $K_2CO_3$. Yield 4.4 g (85%), mp 90–91°C. $^1$H NMR spectrum, δ, ppm: 1.39 s (9H, *t*-Bu), 1.80 m (2H, $ArCH_2CH_2$), 2.27 s [6H, $N(CH_3)_2$], 2.36 t (2H, $CH_2N$), 2.51 t (2H, $ArCH_2$), 6.48 d (1H, $H_{arom}$), 6.78 d.d (1H, $H_{arom}$), 7.01 d (1H, $H_{arom}$), 8.0 br.s (1H, OH). IR spectrum, ν, cm$^{-1}$: 3608 (OH).

Found, %: C 76.28, H 10.25, N 5.30.
$C_{15}H_{25}ON$.
Calculated, %: C 76.55, H 10.70, N 5.52.

***N,N*-Dimethyl-3-(4-hydroxyphenyl)propylamine XV** was prepared similarly from 5.0 g (23.3 mmol) of bromide **V**, 6.4 g of dimethylamine solution (46.5 mmol), and 6.4 g (46.5 mmol) of $K_2CO_3$. The contents of the ampule were transferred into a round-bottomed flask, and the solvent was distilled off on a rotary evaporator. The dry residue was dissolved in ethanol on heating, and the undissolved substance was filtered off. The solvent from the filtrate was distilled off, and the target product was recrystallized from benzene. Yield 2.5 g (61%), mp 114–116°C. $^1$H NMR spectrum, δ, ppm: 1.77 m (2H, $ArCH_2CH_2$), 2.24 s [6H, $N(CH_3)_2$], 2.32 t (2H, $CH_2N$), 2.54 t (2H, $ArCH_2$), 5.05 s (1H, OH), 6.73 d (2H, $H_{arom}$), 7.03 d (2H, $H_{arom}$). IR spectrum, ν, cm$^{-1}$: 3612 (OH).

Found, %: C 73.58, H 9.44, N 7.93.
$C_{11}H_{17}ON$.
Calculated, %: C 73.70, H 9.56, N 7.81.

***N,N*-Dimethyl-3-(4-methoxyphenyl)propylamine XVI** was prepared similarly from 5.7 g (24.4 mmol) of bromide **VI**, 6.7 g of dimethylamine solution (48.8 mmol), and 6.7 g (48.8 mmol) of $K_2CO_3$. Yield 4.0 g (85%), bp 108–110°C (1 mm Hg). $^1$H NMR spectrum, δ, ppm: 1.78 m (2H, $ArCH_2CH_2$), 2.22 s [6H, $N(CH_3)_2$], 2.32 t (2H, $CH_2N$), 2.57 t (2H, $ArCH_2$), 3.70 s (3H, $OCH_3$), 6.85 d (2H, $H_{arom}$), 7.12 d (2H, $H_{arom}$).

Found, %: C 74.28, H 10.03, N 7.55.
$C_{12}H_{19}ON$.
Calculated, %: C 74.57, H 9.91, N 7.24.

***N,N*-Dimethyl-3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propylamine *N*-oxide XVII.** To a solution of 2.0 g (6.9 mmol) of amine **IX** in 15 ml of 2-propanol, we added 0.84 ml (10.3 mmol) of 30% $H_2O_2$. The mixture was stirred at 60°C for 3 h, the solvent was distilled off, and the residue was recrystallized from toluene. Yield 1.9 g (90%), mp 165°C. $^1$H NMR spectrum, δ, ppm: 1.43 s (18H, *t*-Bu), 2.21 m (2H, $ArCH_2CH_2$), 2.60 t (2H, $ArCH_2$), 3.19 s [6H, $N(CH_3)_2$], 3.30 t (2H, $CH_2N$), 5.26 s (1H, OH), 6.99 s (2H, $H_{arom}$). IR spectrum, ν, cm$^{-1}$: 3640 (OH), 954 (NO).

Found, %: C 74.46, H 10.95, N 4.24.
$C_{19}H_{33}NO_2$.
Calculated, %: C 74.21, H 10.81, N 4.56.

***N,N*-Dimethyl-3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propylamine *N*-oxide XVII** was also prepared by oxidation of 2.0 g (6.9 mmol) of amine **IX** with 1.5 ml (10.3 mmol) of an 80% solution of cumene hydroperoxide. The procedure was similar to that described above. Yield 0.9 g (43%).

***N,N*-Diethyl-3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propylamine *N*-oxide XVIII** was prepared similarly by oxidation of 2.0 g (6.3 mmol) of **X** with 0.76 ml of hydrogen peroxide solution (9.4 mmol). Yield 1.7 g (82%), mp 167°C. $^1$H NMR spectrum ($CDCl_3$), δ, ppm: 1.21 s [6H, $N(CH_2CH_3)_2$], 1.37 s (18H, *t*-Bu), 1.98 m (2H, $ArCH_2CH_2$), 2.50 t (2H, $ArCH_2$), 3.00 t (2H, $CH_2N$), 3.10 q [4H, $N(CH_2CH_3)_2$], 5.17 s (1H, OH), 6.84 s (2H, $H_{arom}$). IR spectrum, ν, cm$^{-1}$: 3640 (OH), 948 (NO).

Found, %: C 75.48, H 11.70, N 4.30.
$C_{21}H_{37}NO_2$.
Calculated, %: C 75.17, H 11.11, N 4.18.

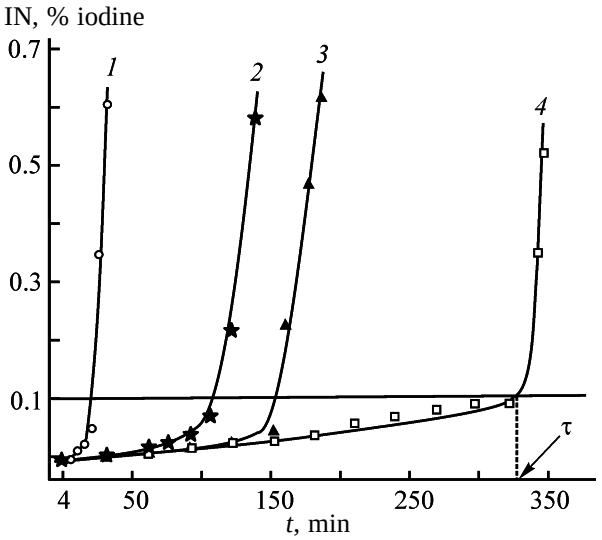
***N,N*-Dipropyl-3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propylamine *N*-oxide XIX was prepared similarly by oxidation of 1.0 g (2.9 mmol) of amine XI** with 0.35 ml of hydrogen peroxide solution (4.3 mmol). Yield 0.8 g (80%), mp 105°C. $^1$H NMR spectrum ($CDCl_3$), δ, ppm: 0.92 t [6H, $N(CH_2CH_2CH_3)_2$], 1.40 s (18H, *t*-Bu), 1.70 m [4H, $N(CH_2CH_2CH_3)_2$], 2.02 m (2H, $ArCH_2CH_2$), 2.52 t (2H, $ArCH_2$), 3.10 t [4H, $N(CH_2CH_2CH_3)_2$], 3.15 m (2H, $ArCH_2CH_2CH_2$), 5.00 s (1H, OH), 6.87 s (2H, $H_{arom}$). IR spectrum, $CHCl_3$, ν, cm$^{-1}$: 3640 (OH), 966 (NO).

Found, %: C 76.03, H 11.54, N 3.93.
$C_{23}H_{41}NO_2$.
Calculated, %: C 75.98, H 11.37, N 3.85.

We also examined the inhibiting activity of 2,6-di-*tert*-butyl-4-methylphenol (Ionol) and *N,N*-dimethyldodecylamine (Acros Organics). Oxidation of lard (Novosibirsk Meat-Canning Plant) was performed under the conditions of oxygen bubbling at 130°C in an oxidation cell similar to that described in [19]. The weight of the lard sample was 50 g, and AO concentration, 1.5 μmol per gram of lard. In the course of the oxidation, 1-g samples of the lard were taken, and the concentration of peroxy compounds was determined by iodometric titration [25]. The kinetic curves were plotted (see figure), and the induction period (time in which the lard was oxidized to a peroxide number of 0.1) was determined graphically. All the measurements were repeated 3–4 times; the mean results with the rms errors are listed in the table.

## CONCLUSIONS

(1) *N,N*-Dialkyl-ω-[4-hydroxy(methoxy)aryl]alkylamines of various structures, forming structurally related series, and their *N*-oxides were prepared.




Kinetic curves of oxidation of lard. Inhibitor: (*1*) none, (*2*) amine **XX**, (*3*) Ionol, and (*4*) amine **IX**. (PN) Peroxide number and (*t*) time.

(2) The aminoalkylphenols synthesized, owing to the bifunctional mechanism of the antioxidative effect and the occurrence of intramolecular synergism, surpass in the inhibiting activity commercial antioxidants and show promise as inhibitors preventing oxidation of fat-containing products.

(3) The inhibiting activity of the aminoalkylphenols synthesized increases with an increase in the distance between the nitrogen atom and aromatic core, decrease in the length of *N*-alkyl substituents, and increase in the extent of steric shielding of the phenolic OH group; in going from aminoalkylphenols to the corresponding *N*-oxides, the antioxidative activity decreases.

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