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Synthesis of *N*-Benzylarylamine Derivatives and Diphenyl Esters of α-Aminomethanephosphonic Acids and Examination of Their Antioxidant Properties

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Abstract—A number of new derivatives of *N*-benzylarylamines and diphenyl α-aminomethanephosphonates have been synthesized, and their structure has been established by IR and ^{1}H NMR spectroscopy. It has been shown that these compounds can be used as effective additives enhancing the thermooxidative stability of ester-based oils.

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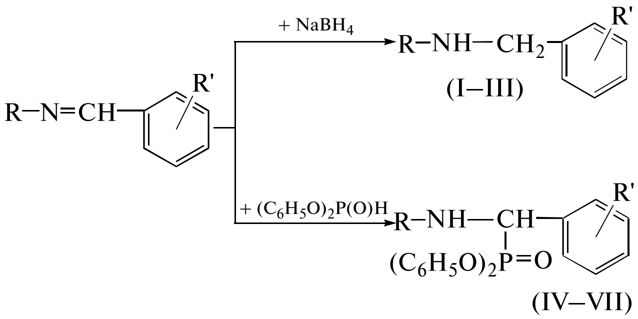
Organic compounds containing the secondary nitrogen atom in combination with various heteroatoms and functional groups are widely used as additives for lubricating oils [1].

In this work, aimed at finding effective antioxidants for ester-based oils, we synthesized and studied new derivatives of *N*-benzylarylamines and diphenyl esters of α-aminomethanephosphonic acids.

EXPERIMENTAL

The compounds of interest were synthesized according to the following schemes:



R = α-$C_{10}H_7$-, R' = *m*-$C_9H_{19}O$- (I); R = $(C_6H_5)_2CH$-, R' = *p*-HO- (II); R = C_6H_5-, R' = $C_6H_5(CH_2)_2O$ (III); R = *p*-$CH_3OC_6H_4$-, R' = *p*-CH_3O- (IV); R = $C_6H_5CH_2$-, R' = *p*-F (V); R = C_6H_5-, R' = *m*-$C_9H_{19}O$- (VI); R = *o*-HOC_6H_4-, R' = *m*-$C_9H_{19}O$- (VII).

The antioxidant activity of the newly synthesized compounds was determined according to GOST (USSR State Standard) 23797-79. Testing was conducted for 20 h at 225°C in the presence of steel, copper, and aluminum plates. The additives were introduced into a pentaerythritol ester of C_5–C_9 synthetic fatty acids (PEE) for a concentration of 0.5%.

The IR spectra of the compounds were recorded on a Spekord M-80 spectrometer as a white oil mull (measurement range, 400–4000 cm^{-1}). Their ^{1}H NMR spectra were recorded on a Brüker AC-300 instrument (operating frequency SF-300, 13 mHz) in DMSO-d_6 solutions with HMDS as an internal standard.

The reactants diphenyl phosphite [2], *m*-nonyloxy- and *p*-phenyloxybenzaledehydes [3], and corresponding azomethines [4] were prepared according to the conventional procedures.

General *N*-benzylarylamines (I–III) synthesis procedure. Sodium borohydride in an amount of 0.11 mol of was gradually added to a stirred solution of 0.1 mol of azomethine in dimethylformamide. The reaction mixture was stirred for 3 h at a temperature of 40–45°C. After cooling, the mixture was poured into 1 l of water and precipitated crystals were filtered off and crystallized from ethyl alcohol.

General procedure for synthesis of diphenyl α-aminomethanephosphonate derivatives (IV–VII). Diphenyl phosphite in an amount of 2.34 g (0.01 mol) was added to a solution of 0.1 mol of azomethine in 5–10 ml of ethanol, and the reaction mixture was stirred at room temperature. Then, the mixture was heated at 60°C over a water bath for 1 h. The product was recrystallized from a 1 : 1 benzene–ethanol mixture, washed with hexane, and dried.

RESULTS AND DISCUSSION

The composition of compounds I–VII was determined on the basis of elemental analysis data, and their structure was confirmed by IR and NMR spec-

Table 1. Physicochemical characteristics and elemental analysis data for the compounds

Compound notation	Compound	Empirical formula	Yield, %	Mp, °C	Found, % Calculated, %			
					N	P	C	H
I	*N*-(*m*-Nonyloxybenzyl)-α-naphthylamine	$C_{26}H_{33}NO$	72	82–84	3.56 3.73	–	83.40 83.15	8.78 8.86
II	*N*-(*p*-Hydroxybenzyl)diphenylmethylamine	$C_{20}H_{19}NO$	90	91–93	4.98 4.98	–	82.83 83.01	6.48 6.62
III	*N*-(p-Phenylethoxybenzyl)aniline	$C_{21}H_{21}NO$	74	67–69	4.54 4.62	–	82.94 83.13	6.79 6.98
IV	Diphenyl ester of α-[(*p*-methoxyphenylamino)-*p*′-methoxyphenylmethane]phosphonic acid	$C_{27}H_{26}NPO_5$	85	115–117	3.12 2.95	6.43 6.52	67.93 68.20	5.57 5.51
V	Diphenyl ester of α-[(benzylamino)-*p*-fluorophenylmethane]phosphonic acid	$C_{26}H_{23}NPO_3F$	65	98–100	3.24 3.13	6.78 6.92	69.60 69.79	5.32 5.18
VI	Diphenyl ester of α-[(phenylamino)-*m*-nonyloxyphenylmethane]phosphonic acid	$C_{30}H_{40}NPO_4$	80	105–107	2.66 2.51	5.37 5.55	73.45 73.22	7.05 7.23
VII	Diphenyl ester of α-[(*o*-hydroxyphenylamino)-*m*'-nonyloxyphenylmethane]phosphonic acid.	$C_{34}H_{40}NPO_5$	78	114–116	2.21 2.24	5.15 5.40	71.35 71.18	7.18 7.03

troscopy. The physicochemical characteristics of the compounds are given in Table 1.

The IR spectra of these *N*-benzylarylamines do not exhibit absorption bands at 1615–1670 cm^{-1} corresponding to stretching vibrations of the –CH=N group and display a distinct band at 3300–3400 cm^{-1} due to stretching vibrations of the NH group.

The ^1H NMR spectrum of *N*-(*m*-nonyloxybenzyl)-α-naphthylamine exhibits proton signals attributed to the following groups (δ): the chemical shifts at 4.45 and 0.9 ppm to the $–N–CH_2–$ and CH_3 groups and the singlet at 1.3 ppm and the triplet at 3.9 ppm to the $–(CH_2)_6–$ and $–O–CH_2–$ moieties, respectively. Aromatic protons are displayed as multiplets in the region of 6.35–7.45 ppm (compound I, Fig. 1).

The IR spectra of diphenyl esters of α-aminomethanephosphonic acids (IV–VII) display absorption bands due to the presence of the NH (3300–3400 cm^{-1}), P=O (1250–1280 cm^{-1}), and P–O–C (1190–1240 cm^{-1}) groups.

The ^1H NMR spectrum of diphenyl α-(4-methoxyphenylamino)-4'-methoxyphenylmethanephosphonate displays proton signals (δ, ppm) due to the following groups: 7.58 d (2H, $A^{(o)}$, J = 9.9 Hz), 7.33 m (2H, $C^{(m)}$, 7.18 t (2H, $C^{(p)}$, J = 7.0 Hz), 7.10 d (2H, $A^{(m)}$, J = 9.0 Hz), 6.88 m (6H, $C^{(o)}$ and $B^{(o)}$), 6.68 d (2H, $B^{(m)}$, J = 9.0 Hz), 6.32 dd (1H, >NH, $J_{CH–NH}$ = 10.8 Hz, $J_{P–CH–NH}$ = 5.5 Hz), 5.42 dd (1H, CH–NH, $J_{P–CH}$ = 25.7 Hz, $J_{CH–NH}$ = 10.8 Hz), 3.72 s (3H, $–OCH_3$ from B), 3.60 s (3H, $–OCH_3$ from A) (compound IV, Fig. 2).

Table 2 presents the results of comparative testing of the synthesized compounds and the commercial additive phenyl-α-naphthylamine (FAN). The compounds are superior to the known inhibitor FAN in all parameters that characterize the extent of oxidation of

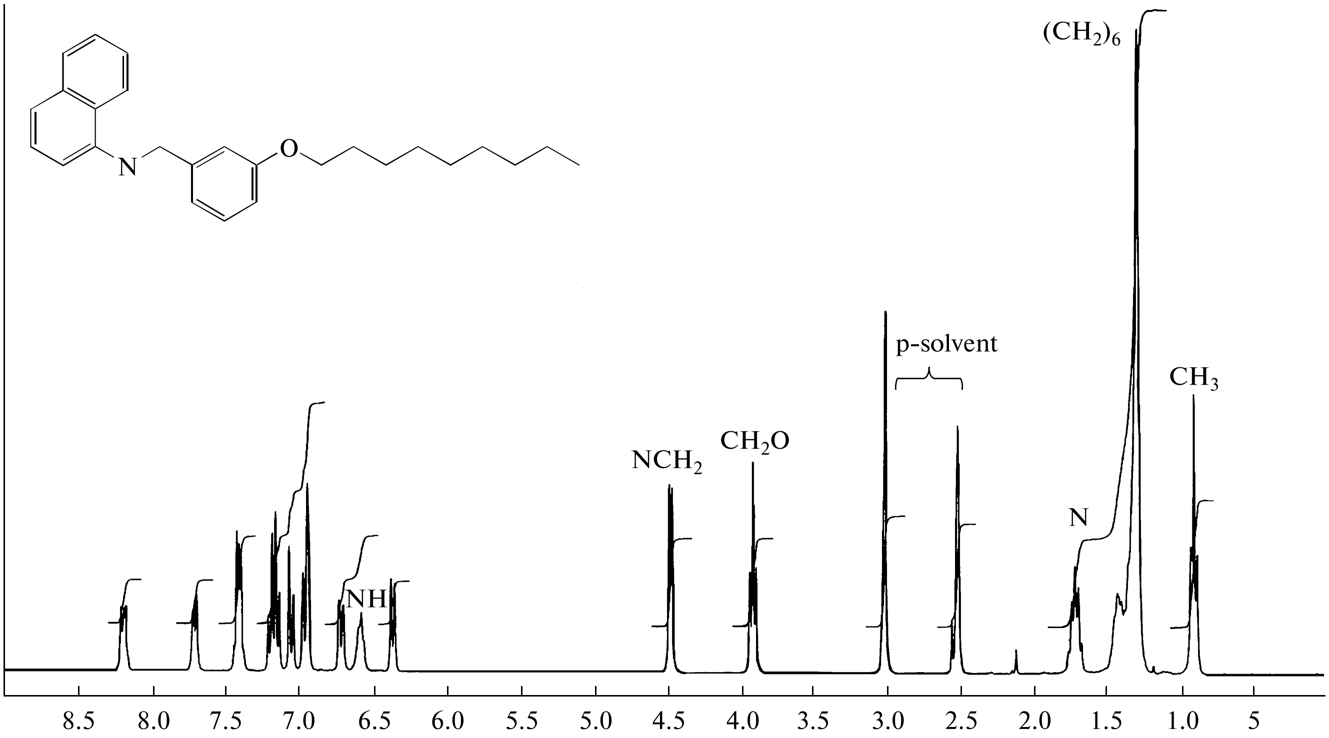


Fig. 1. ^1H NMR spectrum of *N*-(*m*-nonyloxybenzyl)-α-naphthylamine.

synthetic oil (acid number, kinematic viscosity, amount of sediment). There was no corrosion of the metal plates.

The highest performance under the given testing conditions was shown by compounds I and VII, which contain the nitrogen atom in combination with the

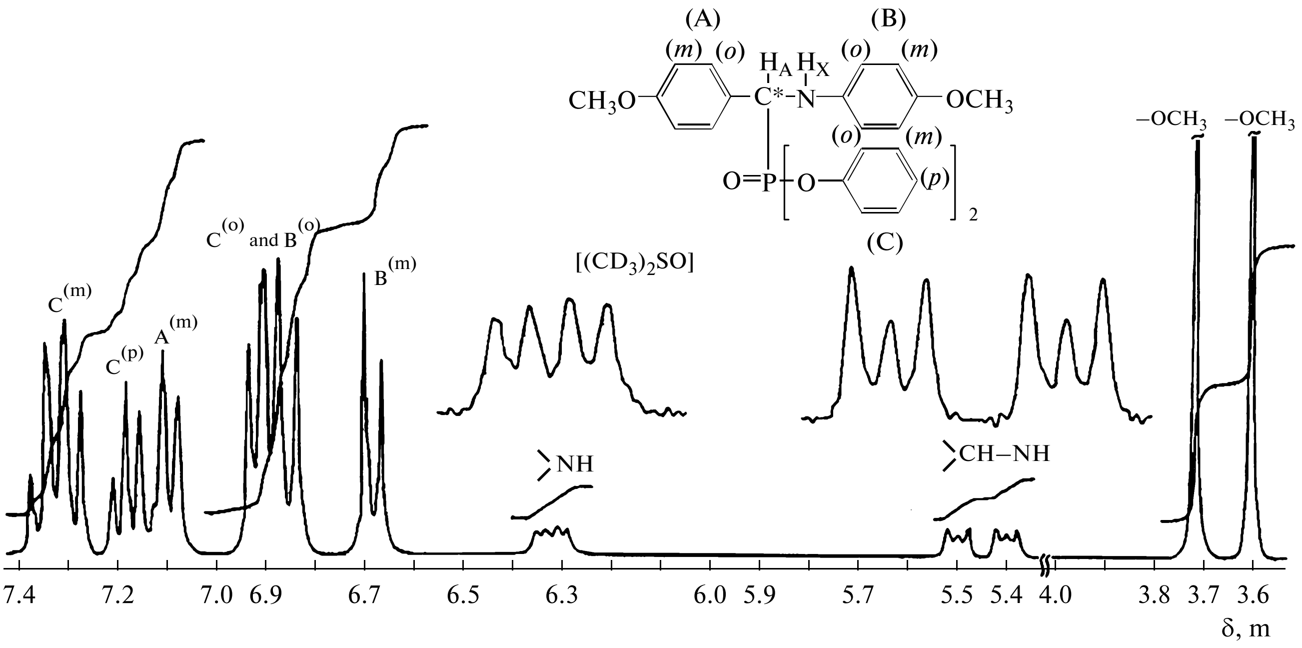


Fig. 2. ^1H NMR spectrum of diphenyl ester of α-[(benzylamino)-*p*'-fluorophenylmethane]phosphonic acid.

Table 2. Effect of the compounds on the thermooxidative stability of pentaerythritol ester at 225°C for 20 h

No.	Additive	After oxidation			
		Amount of sediment, %	Acid number, mg KOH/g	Kinematic viscosity, mm^2/s	
				at 100°C	at –40°C
1	PEE*	0.15	7.6	7.2	38000
2	Phenyl-α-naphthylamine	0.2	4.8	6.45	28000
3	I	0.07	1.4	5.3	20800
4	II	0.11	2.3	5.1	21000
5	III	0.18	2.8	5.5	25200
6	IV	0.16	2.4	5.6	25350
7	V	0.18	2.3	5.4	22000
8	VI	0.12	2.2	5.2	21700
9	VII	0.05	1.6	5.15	20620

* The oil before oxidation had an acid number of 0.4 mg KOH/g and viscosity values of 5.1 mm^2/s and 9850 mm at 100 and –40°C, respectively.

long-chain nonyloxy group. For example, when these compounds were added in an amount of 0.5 wt % to pentaerythritol ester, the kinematic viscosity at –40°C was 20620–20800 mm^2/s and the acid number was 1.4–1.6 mg KOH/g, whereas the application of FAN with the same concentration makes these quantities to be 28000 mm^2/s and 4.8 mg KOH/g, respectively. Compounds II–VI also exhibit good antioxidant properties and do not rank below FAN in performance. Thus, the results allow us to categorize these compounds with promising ester oils capable of operating at 225°C.

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