ISSN 1070-4272, Russian Journal of Applied Chemistry, 2010, Vol. 83, No. 12, pp. 2140–2143. © Pleiades Publishing, Ltd., 2010. Original Russian Text © Ch.K. Rasulov, A.G. Azizov, F.A. Nabiev, S.T. Rustamov, A.S. Askerova, 2010, published in Zhurnal Prikladnoi Khimii, 2010, Vol. 83, No. 12, pp. 2013–2016.

> = ORGANIC SYNTHESIS AND INDUSTRIAL ORGANIC CHEMISTRY

Synthesis of N-[2-Hydroxy-4(5)-methyland -5-(methylcyclohexyl)benzyl]morpholines as Antioxidants for Transformer Oils

Ch. K. Rasulov, A. G. Azizov, F. A. Nabiev, S. T. Rustamov, and A. S. Askerova

Institute of Petrochemical Processes, National Academy of Sciences of Azerbaijan, Baku, Azerbaijan

Received November 26, 2009

Abstract—Aminomethylation of m- and p-cresols and of p-(1-methylcyclohexyl)phenol with formaldehyde and morpholine was studied. The products obtained were tested as antioxidant additives to T-1500 transformer oil.

DOI: 10.1134/S107042721012013X

Alkylphenols and their derivatives steadily attract researchers' attention owing to practical value of these compounds, primarily to very wide spectrum of their antioxidant activity. In particular, numerous patents and articles on this subject have been published in the past decade [1–7].

In this study we performed aminomethylation of mand p-cresols and of p-(1-methylcyclohexyl)phenol with formaldehyde and morpholine and tested the resulting products as antioxidants for transformer oil.

Aminomethylation of *m*- and *p*-cresols and of *p*-(1methylcyclohexyl)phenol with formaldehyde and morpholine can be described as follows:



EXPERIMENTAL

As starting substances we used reagent-grade *m*- and *p*-cresols, formaldehyde (30% formalin), and morpholine.

p-(1-Methylcyclohexyl)phenol was prepared by the reaction of phenol with 1-methylcyclohexene in the presence of acid catalysts [8]. Its characteristics are as follows: bp 160–164°C (1333 Pa), mp 95°C, *M* 190 (exp.).

N-[2-Hydroxy-4(5)-methyl- and 2-hydroxy-5-(methylcyclohexyl)benzyl]morpholines were prepared by the reactions of *m*-, *p*-cresol and *p*-(1-methylcyclohexyl) phenol with formaldehyde and morpholine in 1 : 2 : 2ratio. A three-necked flask was charged with the calculated amounts of the substituted phenol, morpholine, and benzene, and 30% formaldehyde was added dropwise with stirring at 25–30°C, after which the reaction mixture was allowed to stand for 1 h. Then the temperature was gradually raised to 75°C, and the mixture was stirred for another 2 h, after which it was washed with water to remove the unchanged formaldehyde. The amino compounds were separated from alkylphenols by conversion into hydrochlorides.

Then the aqueous solution of the amine hydrochloride was treated with concentrated NH_4OH , and the free amino compound was isolated. The amine was separated from water by extraction with benzene. After distilling the benzene off, the residue was subjected to

Compound	T_{b}	$T_{\rm m}$	Found/ Calculated	Found, %/Calculated, %			Formula
1	°C		М	С	Н	Ν	1
OH H ₃ C CH ₂ -N O	158–160 (666.5 Pa)	60	207/ 207	70.20/ 69.54	8.70/ 8.27	7.30/ 6.76	C ₁₂ H ₁₇ O ₂ N
CH_2 CH_2 OH OH OH OH OH OH OH OH	152–154 (666.5 Pa)	56	207/ 207	70.10/ 69.54	8.45/ 8.27	6.60/ 6.76	C ₁₂ H ₁₇ O ₂ N
OH CH ₂ -NO CH ₃	196–198 (266.6 Pa)	86	289/ 289	75.20/ 74.70	9.60/ 9.40	4.60/ 4.84	C ₁₈ H ₂₇ O ₂ N

 Table 1. Physicochemical parameters of N-benzylmorpholines

fractional distillation in a vacuum, and the physicochemical characteristics and purity of the products were determined. The composition and structure of the products were determined by chromatographic and spectral analysis.

Chromatographic analysis of methyl- and methylcyclohexylphenols and N-benzylmorpholines was performed with an LKhM-72 chromatograph equipped with a thermal conductivity detector. The column length was 2 m. The solid support was Chromaton N-AW-DMC washed with acid and silanized with dimethyldichlorosilane, fraction 0.2–0.25 mm. The stationary phase was 5% methylsiloxane elastomer SE-30. The initial column temperature was 50, and the final temperature, 280°C; the heating rate was 10 deg min⁻¹. The carrier gas was He (flow rate 50 ml min⁻¹). The detector temperature was 300°C. The paper feed rate was 60 mm h^{-1} . The calculations were performed by the method of internal normalization, i.e., the peak areas were calculated relative to their sum taken as 100%.

The IR spectra were recorded with a UR-20 spectrometer, and the ¹H NMR spectra, with a Varian FT-84 device (USA) with HMDS as internal reference. *N*-(2-Hydroxy-4-methylbenzyl)morpholine (I). A three-necked flask was charged with 26.0 g of *m*-cresol, 22.0 g of morpholine, and 100 ml of benzene, after which 25.0 g of a 30% formaldehyde solution was added dropwise. Then the mixture was heated with stirring and worked up as described above. After distillation, the target product was in 70.0% yield.

The physicochemical parameters and elemental composition of I are given in Table 1.

In the ¹H NMR spectrum, the protons of the aromatic ring give signals in the region of 6.3 ppm, and the CH₃ protons, at 0.9 and 1.0 ppm. The integral intensity of the signals at 3.55 and 4.75 ppm is consistent with the number of protons in the substituents CH₂ and $-N < \frac{CH_2}{CH_2}$.

In the IR spectra of the compounds synthesized, the stretching vibrations of C–H groups are manifested at 3000–2800 cm⁻¹, and the phenol OH groups absorbs at 3610 and 1200 cm⁻¹. The bands at 1590 and 1605 cm⁻¹ belong to vibrations of the aromatic ring.

N-(2-Hydroxy-5-methylbenzyl)morpholine (II). A three-necked flask was charged with 26.0 g of *p*-cresol, 22.0 g of morpholine, and 100 ml of benzene, and 25.0 g of a 30% formaldehyde solution was added from a dropping funnel with stirring at 30° C. The

Sampla	Weight fraction of	Resistance to oxidation according to GOST 981–75 and paragraph 5.4 of GOST 982–80			
Sample	precipitate, %	acid number, mg KOH/g	amount of volatile low-molecular- weight acids, mg KOH/g		
Oil without AO	0.8	0.96	0.24		
Oil + Ionol (according to GOST 982–80)	_	0.01	0.04		
Oil + IKhP-21	"	0.09	0.03		
Oil + compound I	"	0.06	0.04		
Oil + compound II	"	Neutral medium	0.03		
Oil + compound III	"	The same	0.02		

Table 2. Results of tests of *N*-benzylmorpholines as AOs for T-1500 transformer oil $[135^{\circ}C, 30 \text{ h}, V(O_2) = 50 \text{ ml min}^{-1}, \text{AO} \text{ amount } 0.4\%]$

subsequent procedure was the same as described above. The target product was obtained in 68.3% yield by vacuum distillation. Its characteristics are as follows: bp $152-154^{\circ}C$ (666.5 Pa), mp 56°C, *M* 207.

The IR and ¹H NMR spectra of *N*-(2-hydroxy-5-methylbenzyl)morpholine are similar to those of **I**.

N-[2-Hydroxy-5-(1-methylcyclohexyl)benzyl]morpholine (III) was prepared similarly to II, starting from 23.7 g of *p*-(1-methylcyclohexyl)phenol, 11.0 g of morpholine, 100 ml of benzene, and 12.5 g of a 30% formaldehyde solution. The target product was isolated by fractional distillation at reduced pressure (2 mm Hg). Its physicochemical characteristics are as follows: bp 196–198°C (266.6 Pa), mp 86°C, *M* 289. Yield 58.7%.

The IR and ¹H NMR spectra of *N*-[2-hydroxy-5-(1methylcyclohexyl)benzyl]morpholine are similar to those of **I**, except that the ¹H NMR signal of the 1.4substituted benzene ring is observed at 6.87 ppm, and the singlet of the CH₃ group, at 1.22 ppm. The integral intensity of the signals at 3.50 and 4.70 ppm is consistent with the number of protons in the substituents CH₂ and $-N < CH_2$. CH₂

The IR absorption spectrum of **III** contains bands at 1505, 1592–1610 (benzene ring), 3010, 3030 (CH₂ stretching vibrations), and 825 cm⁻¹ (out-of-plane bending vibrations of the CH₂ group); the OH group absorbs at 1240 and 3100–3500 cm⁻¹. The gem-

disubstituted cyclohexane ring exhibits C–H stretching vibration bands at 2920 and 2845 cm⁻¹ and the ring CH₂ bending bands at 1108 and 1345 cm⁻¹. The methyl group is characterized by bending vibration bands at 1370 and 1460 cm⁻¹.

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

The synthesized *N*-benzylmorpholines were tested as antioxidants (AOs) for T-1500 transformer oil. We examined the oxidation resistance of the oil without additives and with AOs added, according to GOSTs (State Standards) 981–75 and 982–80. The tests were performed at 135°C for 30 h at an oxygen feed rate of 50 ml min⁻¹. As AOs we tested Ionol, IKhP-21 additive, and the *N*-benzylmorpholines we prepared. The results are given in Table 2.

As can be seen, addition of the *N*-benzylmorpholines to the oil enhances its resistance to oxidation. The best result was obtained with *N*-benzylmorpholines derived from *m*-cresol and *p*-(1-methylcyclohexyl)phenol, with which no precipitate was formed, the acidity was absent, and the amount of volatile lowmolecular-weight acids corresponded to 0.02-0.03 mg KOH/g.

Thus, the compounds we synthesized can be used as effective antioxidant additives to transformer oils.

CONCLUSIONS

(1) N-[2-Hydroxy-4(5)-methyl- and -5-(methylcyclohexyl)benzyl]morpholines were prepared in 58.7– 70.0% yield by aminomethylation of *m*- and *p*-cresols and of *p*-(1-methylcyclohexyl)phenol with formaldehyde and morpholine.

(2) The synthesized products proved to be effective additives to T-1500 transformer oil.

REFERENCES

1. RF Patent 2174506.

- Korenev, D.K., Zavorotnyi, V.A., Kelarev, V.I., and Lagutina, T.A., *Khim. Tekhnol. Topl. Masel*, 2003, nos. 1–3, pp. 61–63.
- Rasulov, Ch.K., Azizov, A.G., Zeinalova, L.B., et al., *Neftekhimiya*, 2006, vol. 46, no. 4, pp. 306–309.
- Prosenko, A.E., Markov, A.F., Khomchenko, A.S., et al., *Neftekhimiya*, 2006, vol. 46, no. 6, pp. 471–476.
- 5. Rasulov, Ch.K., Azizov, A.G., Zeinalova, L.B., et al., *Prots. Neftekhim. Neftepererab.*, 2007, no. 2, pp. 11–15.
- 6. Mamedova, P.Sh., Farzaliev, V.M., and Babaev, E.R., *Neftekhimiya*, 2007, vol. 47, no. 2, pp. 115–119.
- 7. US Patent 6417410.
- 8. Rasulov, Ch.K., Azizov, A.G., and Zeinalova, L.B., *Neftekhimiya*, 2007, vol. 47, no. 6, pp. 442–444.