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Synthesis of Piperazine-1,4-Dipropanoic Acid Di(1,2,2,6,6-pentamethyl-4-piperidine)yl Ester as a Photostabilizer[1]

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Abstract—A new type hindered amine light stabilizer (HALS) has been synthesized. The derivatives of piperazine and piperidine have been combined via the transesterification reaction. Effects of such variables as molar ratio, catalyst dosage, reaction time, and temperature were studied and optimized. The structures of all products were elucidated by FT-IR spectroscopy and NMR spectrometry.

Keywords: hindered amine, light stabilizer, transesterification, piperazine, piperidine

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Rubber materials are indispensable in our daily life [1]. Rubber polymers undergo oxidative degradation under the influence of sunlight throughout their lifetime [2] due to the unsaturated bonds in their chains [3], resulting in the discoloration, cracking, stiffening, and decrease in the physico-mechanical and chemical ies of rubber characteristics that make their service life shorter resulting in negative influence on the environment [4]. Maintaining of the unique properties of rubber polymers for longer time can be achieved by blending in a small quantity of a stabilizer [5].

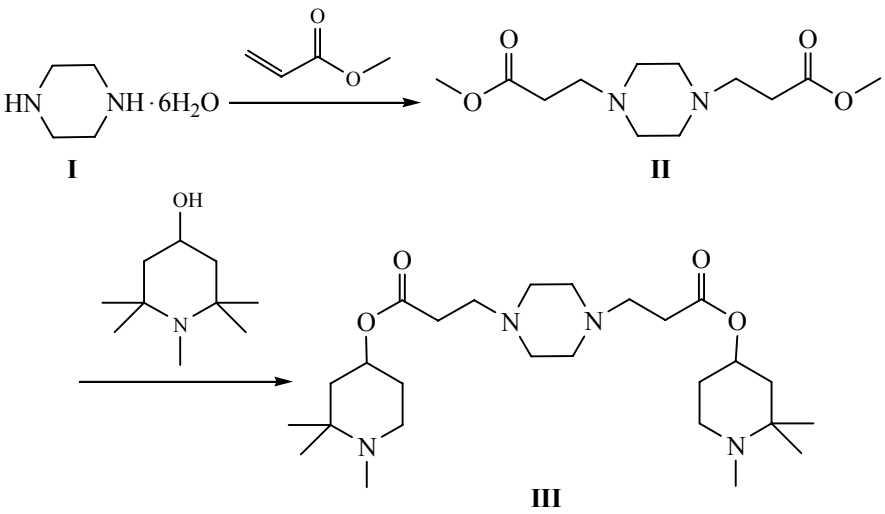
Among the efficient light and heat stabilizers are those of HALS type that are predominantly derivatives of 2,2,6,6-tetramethyl piperidine [6–9]. They form nitroxide radicals either reacting with peroxy radicals or occasionally with atmospheric oxygen [10, 11]. The nitroxide radicals can regenerate and capture alkyl radicals efficiently retarding the degradation process [12, 13]. HALS can be classified as the derivatives of piperidine, piperazine and imidazolidazolidinone depending on the structure of a parent molecule [14]. Compared to piperidine derivatives piperazine derivatives have some advantages: (1) low alkalinity, (2) high compatibility with resin, (3) weak interactions with other acidic components in the system, (4) high thermal and oxygen resistance. Combined together in a compound these exhibit pronounced synergic stabilizing effect [15] making application scope of a new stabilizer much broader.

In order to combine the derivatives of piperidine and piperazine in the same molecule we designed and successfully synthesized piperazine-1,4-dipropanoic acid di(1,2,2,6,6-pentamethyl-4-piperidine)yl ester via transesterification of piperazine-1,4-dipropanoic acid diemthyl ester with 1,2,2,6,6-pentamethyl-4-piperidinol (Scheme 1). Transesterification of the ester with piperidinol is more complicated than with aliphatic alcohols due to the stereo structure of piperidinol.

Effect of substrate molar ratio. The molar ratio of substrates, namely piperazine-1,4-dipropanoic acid dimethyl ester to 1,2,2,6,6-pentamethyl-4-piperidinol had an impact on the yield of the process (Table 1) due to specific features of transesterification. The reaction can be shifted to the right applying an excess of 1,2,2,6,6-pentamethyl-4-piperidinol and removing small molecular weight byproducts. Methanol can be removed efficiently by 3A molecular sieves.

Effect of catalyst loading. The catalyst was studied in the rate range from 1.0% to 3.0% (w/w of substrates) under otherwise similar conditions.

[1] The text was submitted by the authors in English.



Scheme 1. Synthesis of piperazine-1,4-dipropanoic acid di(1,2,2,6,6-pentamethyl-4-piperidine)yl ester.

According to Table 2, the yield increased with an increase in the catalyst loading from 1.0% to 3.0% gradually. 2.0% CH_3ONa was singled out as an optimum rate in the process.

Effect of temperature. Heating improved the rate of conversion of piperazine-1,4-dipropanoic acid dimethyl ester and 1,2,2,6,6-pentamethyl-4-piperidinol in the endothermic reaction (Table 3). The yield increased from 86.2% to 92.0% within the temperature range 120 to 150°C The temperature 150°C was maintained in the subsequent experiments.

Effect of reaction time. Yield of the product gradually increased with longer reaction time. But it did not improve after 12 h of heating probably due to an equilibrium of the reaction reached (Table 4).

EXPERIMENTAL

All chemicals and solvents were used without additional purification unless otherwise specified. Toluene was distilled freshly over benzophenone-sodium. 3A molecular sieves were activated by heating. TLC was performed on GF_{254} glass-backed silica gel plates and visualized in an iodine chamber. NMR was recorded by a Bruker AVANCE 600 spectrometer [^{1}H (600 MHz) ^{13}C (151 MHz)], Switzerland, in $CDCl_3$ with TMS as an internal standard. FT-IR were recorded in the solid state as KBr pellets by a Spectrum One (Version BM) spectrometer of US PE Instrument Company. Elemental analyses was carried out by a Vario EL CUBE of Elementar Analysensysteme GmbH.

Piperazine-1,4-dipropanoic acid dimethyl ester (II). A mixture of piperazine hexahydrate (0.1942 g, 1 mmol), methyl acrylate (0.2152 g, 2.5 mmol) and graphene oxide dispersion in water (5 mL) were loaded in a 50 mL three-neck round-bottom flask. The reaction mixture was vigorously stirred at room temperature for 30 min. Progress of the reaction was

Table 1. Effect of *n*(ester) : *n*(alcohol) ratio on transesterification. Reaction conditions: *n*(ester) : *n*(alcohol) = 1 : 2.2, 150°C, 12 h

n(ester) : *n*(alcohol)	Yield, %
1 : 2.0	88.3
1 : 2.1	91.2
1 : 2.2	92.6
1 : 2.3	92.8
1 : 2.4	92.9

Table 2. Effect of the catalyst rate on transesterification. Reaction conditions: *n*(ester) : *n*(alcohol) = 1 : 2.2, 150°C, 12 h

Catalyst mass fraction, %	Yield, %
1.0	81.6
1.5	88.7
2.0	92.0
2.5	92.4
3.0	92.6

Table 3. Effect of the reaction temperature on transesterification. Reaction conditions: ω(CH_3ONa) = 2.0%, *n*(ester) : *n*(alcohol) = 1 : 2.2, 12 h

Temperature, °C	Yield, %
120	86.2
130	89.1
140	90.8
150	92.0
160	92.1

Table 4. Effect of reaction time on transesterification. Reaction conditions: ω(CH_3ONa) = 2.0%, *n*(ester) : *n*(alcohol) = 1 : 2.2, 12 h

Time, h	Yield, %
8	83.7
10	89.2
12	92.0
14	92.2
16	92.3

monitored by TLC. Upon completion of the procesrs the reaction mixture was extracted repeatedly with ethyl acetate and the organic lay dried over anhydrous sodium sulfate and concentrated in vacuum to yield a white solid compound. FT-IR, ν, cm^{-1}: 2957, 2873, 1379 (CH_3), 2940, 2829, 1460 (CH_2), 1733 (C=O), 1265 (C–O), 1149 (C–O–C), 1195 (C–N). ^{1}H NMR spectrum, δ, ppm: 3.67 s (6H, CH_3), 2.68 d.d (4H, CH_2C=O), 2.55–2.35 m [12H, $(CH_2)_2NCH_2$]. ^{13}C NMR spectrum, δ_C, ppm: 32.13, 51.66, 52.90, 53.55, 172.92. Found, %: C 56.04; H 8.37; N 24.80; O 10.79. $C_{12}H_{22}N_2O_2$. Calculated, %: C 55.80; H 8.58; N 24.78; O 10.84.

Piperazine-1,4-dipropanoic acid di(1,2,2,6,6-pentamethyl-4-piperidine)yl ester (III). Piperazine-1,4-dipropanoic acid dimethyl ester (0.2585 g, 1.002 mmol), 1,2,2,6,6-pentamethyl-4-piperidinol (0.3781 g, 2.208 mmol), toluene (10 mL), CH_3ONa (0.0127 g, 0.2356 mmol, 2% of the total amount of reactants) and 3A molecular sieves were loaded in a 50 mL round bottom flask the reaction mixture was refluxed at 150°C for 12 h. The reaction was monitored by TLC. Upon completion of the reaction the solvent was evaporated in vacuum and the residue washed with hot water. The organic layer was separated and the aqueous phase extracted with ethyl acetate. The combined extracts and organic phase were dried over sodium sulfate and concentrated under vacuum. The product was recrystallized from hot petroleum ether in the form of a white solid. FT-IR, ν, cm^{-1}: 2972, 1349 (CH_3), 2806, 1457 (CH_2), 1728 (C=O), 1298 (C–O), 1008 (C–O–C), 1239, 1192 [$C(CH_3)_2$], 1181 (C–N). ^{1}H NMR spectrum, δ, ppm: 5.04 t.t (2H, piperidine CH), 2.67–2.63 m (4H, CH_2–C=O), 2.62–2.34 m [12H, $(CH_2)_2NCH_2$], 2.22 s (6H, N–CH_3), 1.82 d.d (4H, piperidine CH_2), 1.45 t (4H, piperidine CH_2), 1.15 s (12H, piperidine CH_3), 1.06 s (12H, piperidine CH_3). ^{13}C NMR spectrum, δ_C, ppm: 20.88, 26.20, 32.80, 33.24, 45.96, 52.99, 53.72, 55.45, 67.90, 172.30. Found, %: C 67.05; H 10.48; N 10.32; O 12.15. $C_{30}H_{56}N_4O_4$. Calculated, %: C 67.13; H 10.52; N 10.44; O 11.92.

CONCLUSIONS

Piperazine–1,4-dipropanoic acid di(1,2,2,6,6-pentamethyl-4-piperidine)yl ester was successfully synthesized in the process of transesterification. The optimum reaction conditions were 150°C, reaction time 12 h, CH_3ONa rate 2.0% (w/w of substrates), and 1 : 2.2 ester : alcohol molar ratio, toluene media with 3A molecular sieves. The optimal condition led to the yield 92.0%.

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REFERENCES

1. Reingruber, E. and Buchberger, W., *J. Sep. Sci.*, 2010, vol. 33, p. 3463.
2. Bojinov, V.-B. and Grabchev, I., *Polym. Degrad. Stab.*, 2001, vol. 74, p. 543.
3. Narathichat, M., Sahakaro, K., and Nakason, C., *J. Appl. Polym. Sci.*, 2010, vol. 115, p. 1702.
4. You, B., Zhou, D., Yang, F., and Ren, X.-C., *Colloids Surf. A*. 2011, vol. 392, p. 365.
5. Singh, R.-P., Vishwa Prasad, A., and Pandey, J.-K., *Macromol. Chem. Phys.*, 2001, vol. 202, p. 672.

6. Jia, H.-S., Wang, H.-L., and Chen, W.-X., *Radiat. Phys. Chem.*, 2007, vol. 76, p. 1179
7. Schaller, C., Rogez, D., and Braig, A., *J. Coat. Technol. Res.*, 2009, vol. 6, p. 81.
8. Kosa, C.-S. Chmela, Š., Pawelke, B., Theumer, G., and Habicher, W.-D., *Polym. Degrad. Stab.*, 2003, vol. 81, p. 453.
9. Mosnáček, J., Bertoldo, M., Kósa, C., Cappelli, C., Ruggeri, G., Lukáč, I., and Ciardelli, F., *Polym. Degrad. Stab.*, 2007, vol. 92, p. 849
10. Bojinov, V. and Grabchev, I., *J. Photochem. Photobiol. A*, 2002, vol. 146, p. 199.
11. Bojinov, V.-B.*, Polym. Degrad. Stab*., 2006, vol. 91, p. 128.
12. Zeynalov, E.-B. and Allen, N.-S., *Polym. Degrad. Stab.*, 2006, vol. 91, p. 3390.
13. Gryn'ova, G., Ingold, K.-U., and Coote, M.-L., *J. Am. Chem. Soc.*, 2012, vol. 134, p. 12979.
14. Wu, W.-E., Chen, K.-X., Zhu, X.-E., and Hua, D., *Fine Chem.,* 1997, vol. 14, p. 6 (in chinese).
15. Cibulková, Z., Černá, A., Šimon, P., Uhlár, J., Kosár, K., and Lehocký, P., *J. Therm. Anal. Calorim.*, 2012, vol. 108, p. 415.