Synthesis of Bis (2,2,6,6-tetramethyl-4-piperidinyl) Maleate

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Abstract: Bis (2,2,6,6-tetramethyl-4-piperidinyl) maleate is a key intermediate for the synthesis of new types of hindered amine light stabilizers (HALS), so new synthetic routes to this compound are desirable. Through an orthogonal design and follow-up single factor experiments optimal reaction conditions were determined for synthesizing bis (2,2,6,6-tetramethyl-4-piperidiny) maleate using dimethyl maleate, 2,2,6,6-tetramethyl-4-piperidinol and zeolite supported tetraisopropyl titanate as catalyst. Under the selected conditions, the reaction rate and the yield are high, the selectivity is good, the catalyst can be recycled, and there are fewer wastes. The product was characterized and quantitatively analyzed by elemental analysis, mass spectrometry, infrared spectroscopy, nuclear magnetic resonance spectroscopy and ion suppression chromatography.

Keywords: Bis (2,2,6,6-tetramethyl-4-piperidinyl) maleate; molecular synthesis

Introduction

Many polymers deteriorate rapidly when they are exposed to sunlight. In order to solve this problem numerous light stabilizers have been developed. Hindered amine light stabilizers (HALS) have the characteristics of high efficiency, heat-resistance, fastness to extraction, non-toxicity, and compatibility with antioxidants. Therefore, HALS are widely used in the synthesis of many polymers, such as polypropylene, polyethylene, polystyrene, polyvinylchloride, polyamides, polyesters, polyacetals, polyurethanes, and so on [1].

   Bis (2,2,6,6-tetramethyl-4-piperidinyl) maleate (BPM) is a key intermediate for preparing new types of HALS and several synthesis methods have been reported [2~4]. In this paper, a new preparation of BPM from dimethyl maleate (DMM) and 2,2,6,6-tetramethyl-4-piperidinol (TMP) in a mixture of dimethylbenzene-ethylbenzene (DE) is discussed. Zeolite supported tetraisopropyltitanate (TESZ) was selected as the catalyst for the new method. With the new method, the synthesis is fast and gives high yields; also the catalyst can be recovered. The products were characterized by their infrared, mass spectrum and nuclear magnetic resonance spectra.

Results and Discussion

Research on Influencing Factors

   Numerous factors may influence an organic reaction. In the synthesis of BPM, the rate of production Y is determined by the following factors: the type of raw materials (A), the reaction temperature (B), the reaction time (C), the mixture ratio (D), the stirring rate (E), the type of catalyst (F), the level of catalyst usage (G) and the rate of distillation of the methanol produced (H). For the orthogonal design, the number of levels of A was set at 2, i.e. dimethyl maleate (DMM) and diethyl maleate (DEM). The number of levels of F was defined as 3: tetraisopropyl titanate (TE), zeolite supported tetraisopropyltitanate (TESZ) and tetraisopropyltitanate supported on activated charcoal (TESA). The number of levels of other factors was also set at 3. The levels of all factors studied are summarized in Table 1. The experimental plan is designed according to an $L_{18}(2^1 \times 3^7)$ orthogonal layout. The rate of the production Y is the target for optimization. Y is calculated by

$$Y = \frac{the\ yield\ of\ BPM\,(mol)}{the\ input\ quantity\ of\ DMM\,(mol)} \times 100\% \tag{1}$$

and the results are shown in Table 2.

Table 1. The factor levels for the synthesis of BPM

Factor	A	B ^{o}C	C H	D^{a}	E rev/min	F	G^{b}	H d/min
level 1	DEM	140	20	0.50	800	TE	0.001	0.25
level 2	DMM	110	14	0.45	400	TESZ	0.005	0.50
level 3	-	153	8	0.40	100	TESA	0.010	1.00

[a]D is the mole ratio of DEM (or DMM) and TMP

[b]G is the mole ratio of TE and pure DEM (or DMM)

Table 2. The orthogonal design layout and the experimental results

No.	A	B	C	D	E	F	G	H	Y
1	DEM	140	20	0.40	400	TESZ	0.001	0.50	53.1
2	DEM	110	20	0.50	800	TE	0.005	0.25	45.5
3	DEM	153	20	0.45	100	TESA	0.010	1.00	13.6
4	DEM	140	14	0.45	800	TESZ	0.010	0.25	86.3
5	DEM	110	14	0.40	100	TE	0.001	1.00	30.9
6	DEM	153	14	0.50	400	TESA	0.005	0.50	14.6
7	DEM	140	8	0.50	100	TE	0.010	0.50	82.5
8	DEM	110	8	0.45	400	TESA	0.001	0.25	10.6
9	DEM	153	8	0.40	800	TESZ	0.005	1.00	15.2
10	DMM	140	20	0.50	800	TESA	0.001	1.00	20.2
11	DMM	110	20	0.45	100	TESZ	0.005	0.50	75.9
12	DMM	153	20	0.40	400	TE	0.010	0.25	24.9
13	DMM	140	14	0.40	100	TESA	0.005	0.25	38.9
14	DMM	110	14	0.50	400	TESZ	0.010	1.00	80.9
15	DMM	153	14	0.45	800	TE	0.001	0.50	16.6
16	DMM	140	8	0.45	400	TE	0.005	1.00	82.9
17	DMM	110	8	0.40	800	TESA	0.010	0.50	20.2
18	DMM	153	8	0.50	100	TESZ	0.001	0.25	26.2
sum of level 1	352.3	363.9	233.2	269.9	204.0	283.3	157.6	232.4	
sum of level 2	376.7	264.1	268.2	285.9	267.0	337.6	273.0	262.9	
sum of level 3		111.1	228.6	183.2	268.0	118.1	308.4	243.7	
difference between levels	24.4	252.8	39.6	102.7	64.0	219.5	150.8	30.5	

It may be deduced from Table 2 that the factors can be ranked according to their influence on Y as follows: B, F, G, D, E, C, H and A. From the orthogonal experimental results, the initial optimal reaction conditions are

A: DMM; B: 140 ^{o}C; C: 14 h; D: 0.45; E: 100; F: TESZ; G: 0.01; H: 0.50

Factors A, H and E can be negligible. B is an important factor, but 140 ^{o}C is the reflux temperature of xylene mixtures and B is 140 ^{o}C. Thus G, D and C were further studied as single variable factors under the conditions determined. The results are shown in Tables 3~5.

Table 3. Influence of the catalyst level (G) on Y

G	0.008	0.010	0.012	0.014	0.016	0.018
Y	70.1	80.2	86.5	91.8	93.2	94.3

Table 4. Influence of the raw material ratio (D) on Y

D	0.50	0.48	0.44	0.42	0.39	0.32
Y	74.1	80.1	83.6	86.2	87.3	88.1

Table 5. Influence of the reaction time (C) on Y

C	6	8	12	16	20	25
Y	77.1	86.3	88.6	92.9	83.3	76.7

It is clear from Tables 3~5 that Y increases with G., but the rate of the increase flattens. When economic costs are considered, the optimum value is G=0.016. Y decreases as D increases and for the same economic reasons, the optimum value is D=0.40. Based on the results is Table 5, a 16h reaction time was selected as the best.

Using the optimal reaction conditions determined by the orthogonal experiments and the follow-up single factor experiments, the reaction was then repeated 8 times. The average value of Y for these runs was 93.4%.

Catalyst usage

TESZ catalyst has high activity and good selectivity, but it will become inactive when wetted, therefore, it must be protected from water during storage and use. If the catalyst is protected from water, the activity and selectivity do not deteriorate after recycling 5 times. It should be pointed out that once TESZ is deliquesced, it would be inactivated forever.

Conclusions

Through an orthogonal design and follow-up single factor experiments, the optimal reaction conditions for synthesizing bis (2,2,6,6-tetramethyl-4-piperidiny) maleate using dimethyl maleate and 2,2,6,6-tertramethyl-4-piperidinol with zeolite supported tetraisopropyltitanate as catalyst were determined. Under the selected conditions, the reaction rate and the yields are high, the selectivity is good, the catalyst can be recycled, and there are few wastes. The product was characterized by elemental analysis, mass spectrometry, infrared spectroscopy and nuclear magnetic resonance spectroscopy.

Experimental

General

LC-6A HPLC, XRC-1 micromeldometer, L-200SM electronic balance, HP5988A high-resolution mass spectrometer, RFO-65 infrared spectrometer, Unity-400 ^{1}H-NMR spectrometer

and PE-2400 elemental analyzer were used in the experiments. Dimethyl maleate (purity≥99.8%) was obtained from Lab-scan ASIA Ltd. (Thailand), 2,2,6,6-tetramethyl-4-piperidinol (purity≥98.0%) was obtained from Peking Third Chemical Factory (China), dimethylbenzene-ethylbenzene (DE) mixture from the Peking Chemical Factory (China) was used (mole fraction of ethylbenzene = 20%). Nitrogen (purity≥99.999) was provided by Peking Praxair Gas Ltd. (China). The zeolite supported tetraisopropyl titanate catalyst was prepared by the authors.

Synthesis and characterization of products.

Bis(2,2,6,6-tetramethyl-4-piperidinyl) maleate is synthesized from dimethyl maleate and 2,2,6,6-tetramethyl-4-piperidinol as indicated in the following reaction scheme:
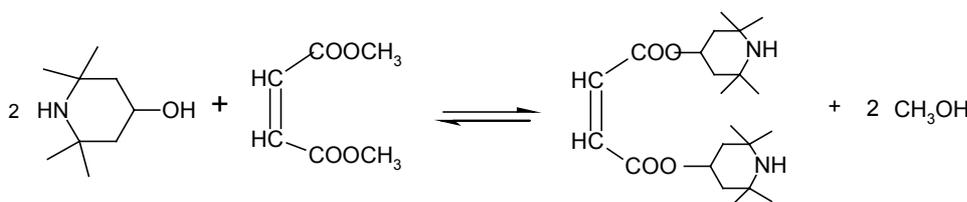
Weighed amounts of DE, DMM and TMP were placed in a three-necked flask. High-purity nitrogen was used as blanketing gas. With stirring and under nitrogen, the reaction mixture was heated slowly to reflux. The temperature at the top of the fractionation column was maintained at about 60 ^{o}C to continuously remove the methanol produced. After the reaction was finished, the reaction mixture was filtered while hot and the catalyst was recycled. The filtrates were distillated under vacuum to recover the solvent. Then the residues were recrystallized from *n*-hexane to obtain pure BPM. The product is a white lamellar crystal and its melting point is in the 80.3~81.6 ^{o}C range. The product was analyzed by ion suppression chromatography and shown to contain no detectable impurities [5, 6]. ^{1}H-NMR (CDCl$_3$, δ): 6.20 (2H, s, =C-H), 5.30 (2H, m, H-C-O), 2.00 (4H, dd, J=12.0, 3.2 Hz, -CH$_2$-), 1.26, 1.17 (each 12H, s, CH$_3$), 1.22 (2H, s, >NH), 1.19 (4H, s, -CH$_2$-); IR (KBr, v_{max}/cm^{-1}): 3312 (NH), 2973, 2941, 2856 (CHCH$_2$) 1711 (C=O), 1633 (C=C), 1381 (CH$_3$), 1245 (COO), 1183 (C-O-C); MS (%): 394 (M$^+$, 1), 379 ([M-CH$_3$]$^+$, 2), 124 ([(CHCH$_2$CNHCCH$_2$) COO]$^+$, 100), 58 ([CHCOOH]$^+$, 47), 41 ([CH$_2$CNH]$^+$, 16).

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Sample Availability: Samples are available from the authors.