Processes of petrochemistry and oil-refining, *2014, vol 15, № 3(59), p.214-222.*

UDC: 547.425:547.464:547.569

SOME PROPERTIES OF ACYLATION REACTION OF PARA-(1-(CYCLOHEX-3-EN-1-YL)ETHYL)PEHOL WITH ACETIC ACID

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Received: 19.05.2014.

In this research , we examined the synthesis of para-(1-(cyclohex-3-en-1-yl)ethyl)pehol from the alkylation reaction of phenol with vinylcyclohexene in the presence of zeolite Y, impregnated with o-phosphoric acid and acylation reaction of this phenol derivative with acetic acid in the presence of $ZnCl_2$

Key words: *phenol, 3-vinylcyclohexene, catalyst, alkylation, acetic acid, acylation, yield, selectivity*

Para-alkylphenols are the raw material of the synthesis of chemical additives as antioxidants, stabilizer to polyolefins , rubbers ,oils and fuels [1-5]. For this reason alkyl group in para-alkylphenols is displaced with other alkyl groups, it is possible to synthesis efficient chemical additives [6-9].

In this article we mentioned the synthesis of para-(1-(cyclohex-3-en-1-yl)ethyl)pehol from the alkylation reaction of phenol with 3-vinylcyclohexene in the presence of zeolite Y, impregnated with o-phosphoric acid and acylation reaction of this phenol derivative with acetic acid in the presence of $ZnCl_2$.

EXPERIMENTAL PART

The process of the synthesis of 1-(5-(1-(cyclohex-3-en-1-yl)ethyl)-2-hydroxyphenyl)-ethanone occurs in two steps .

1^{st} step : Alkylation reaction of phenol with 3- vinylcyclohexene

For the alkylation reaction , phenol and 3-vinyl cyclohexene were used as raw materials and zeolite Y, impregnated with o-phosphoric acid was used as a catalyst . Phenol was purified with distillation before using in the reaction. 3-vinylcyclohexene was synthesized from the cyclodimerization of divinyl[10].For process , 98.8 -99.0% pure 3-vinylcyclohexene was obtained .mp:130^0C, n^{20}_D : 1.4648 , ρ^{20}_4 : 0.8308 , molar mass : 108 g/ mole.

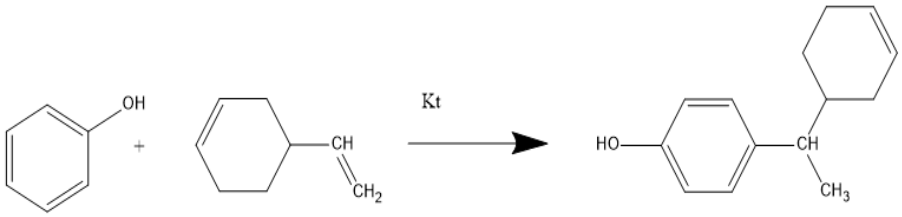
A catalyst on o-phosphoric acid base was prepared by thorough mixing of alumogel with cracking catalyst-zeolite of Y type (SiO_2/Al_2O_3 4,8, ionic exchange degree 97 %). The mass obtained was moulded, pressing through drawing nozzle (with diameter 1.6 mm), granulated and calcined. Then catalyst was impregnated with 10 % solution of phosphoric acid, evaporated, dried in furnace at 100 °C and calcined by temperature rise from 200 to 600 °C.After cooling it is ready to be used .

The procedure of the alkylation reaction of phenol with 3-vinylcyclohexene : phenol and catalyst were put into three-necked round bottom flaks and were heated. When the temperature reached to 40^{o}C , 3-vinylcyclohexene was added dropwise into mixture while stirring. Mixture was stirred for 2 - 5 hours at 60 ^{o}C -120 ^{o}C. Then at 45 ^{o}C it was filtered to seperate the catalyst .It was rectificated and the product was distilled under reduced pressure .

The product obtained was rectified and analyzed using physico-chemical, spectroscopic and chromatographic methods.

RESULTS AND DISCUSSION

The scheme of the reaction of phenol with 3-vinylcyclohexene in presence of zeolite Y, impregnated with o-phosphoric acid as a catalyst :



To obtain good yield of para-(1-(cyclohex-3-en-1-yl)ethyl)pehol ,we made a research on temperature between 60 ^{0}C and 120 ^{0}C , duration between 2 and 6 hours , mol fractions of pehols to 3-vinylcyclohexene 0.5÷1:3 and amount of catalyst :5-20 % about the reaction .

The results of the alkylation reaction of phenol with 3-vinylcyclohexene in the presence of zeolite Y, impregnated with o-phosphoric acid as a catalyst was given in Table -1.

According to table-1, percentage yield of product was 40.2 -72.4 % (according to phenol) at 60 ^{0}C -90^{0}C and the selectivity was 89.3-95.7% (for he product).When the temperature increased to 100 ^{0}C , percentage yield of product is 81.6 % and the selectivity is 97.3 % . If the temperature increased up to 120 ^{0}C , the percentage of yield and selectivity decreased .When duration of the reaction was 4 hours ,the percentage yield was 81.6% .If the duration was increased to 6 hours , the percentage yield became 88.4% .2 or 3 hours was not enough for the alkylation for this reason percentage yield was 41.6 % and 58.7% and selectivity was 95.2 % - 96.5% .From the table ,to increase the convection of 3-vinylcyclohexene , mole ratio of reactants was 1:1 mole .Increasing or decreasing the amount of phenol or 3-vinylcyclohexene did

not obtain good yield and caused it to decrease the selectivity because of the formation of by-products.The amount of catalyst was 7% by mass of phenol to obtain good yield (81.6%).When the amount was increased 10-15 % , the percantage yield incerased 2-3% and it is not economical.

The optimum reaction conditions for the good yield : temperature at 100 ^{0}C , duration : 4 hours, mole ratio of reactants 1:1mole/mole ,mass of catalyst 7% by mass of phenol.According to them , the percantage yield of reaction was 81.6% and selectivity on phenol was 97.3 %.

The structure of para-(1-(cyclohex-3-en-1-yl)ethyl)pehol was proved by using IRand PMR- spectrum.

In IR-spectrum of para-(1-(cyclohex-3-en-1-yl)ethyl)pehol the following typical absorption bands are observed: 1505,1592 – 1610 cm^{-1} (phenyl ring) , 3010,3030 cm^{-1} (valency shift)1240 cm^{-1} and 3100 3500 cm^{-1} (OH group), 2920 and 2845 cm^{-1} (the gem substituted CH groups of cyclohexene ring),1108 and 1345 cm^{-1} (δ_{CH2} in cyclic structure) ,1370 and 1460 sm^{-1} (deformation vibration of C–H bond in CH_3 and CH_2 groups).

In table 2 , there is physico-chemical characteristics and mass percentage of elements of para-(1-(cyclohex-3-en-1-yl)ethyl)pehol.

Table 2. The physico-chemical characteristics of para-(1-(cyclohex-3-en-1-yl)ethyl)pehol

Structure formula	bp, °C	n_D^{20}	ρ_4^{20}	Molecular mass		Mass percentage of elements			
				Cald.	Found	Calculated		Found	
						C	H	C	H
	147-148	1.5445	1.0040	202	202	83.2	8.9	83.9	9.4

From the alkylation reaction of phenol with 3-vinyl cyclohexene , we can obtain 2-mono , 2,4- , 2,6-di and 2,4,6- tri substituted cyclohexenylphenols and if excess phenol is used , cyclobisphenol is obtained.

The products of alkylation reaction could be isolated by distillation in different methodsand their chemical structures and physico-chemical properties were indentified.

2^{nd} step : The acylation reaction of para-(1-(cyclohex-3-en-1-yl)ethyl)pehol with acetic acid

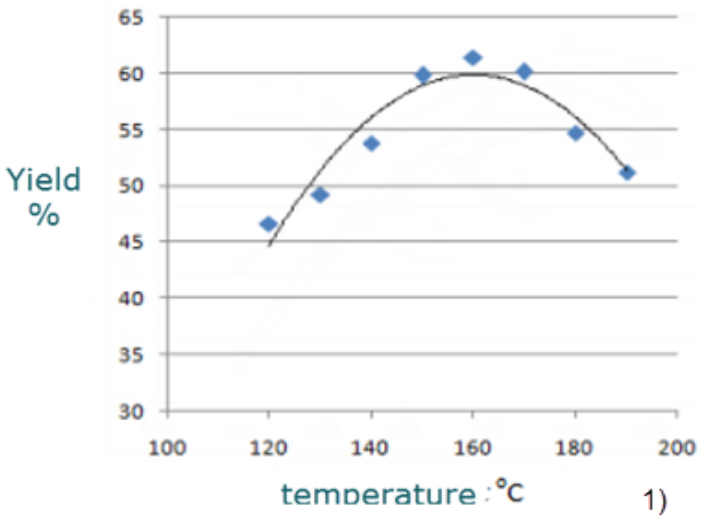
The acylation reaction of para-(1-(cyclohex-3-en-1-yl)ethyl)pehol with acetic acid in the presence of $ZnCl_2$ occurred .

Para-(1-(cyclohex-3-en-1-yl)ethyl)pehol and acetic acid was used as a raw materials. Acetic acid used as a chemical purifier .The physic-chemical properties of acetic acid : bp=118 ^{o}C, mp=16.8 ^{o}C ,molecular weight = 60 g/ mole

Anhydrous $ZnCl_2$ was used as a catalyst.

The reaction was done a method which is given below :

16.5 g (0.12 mol) anhydrous $ZnCl_2$ and 16.5 g (0.27) glacial acetic acid filled into a flask and heated. When the tempurature became 100 °C, 20.2 g (0.1 mol) para-(1-(cyclohex-3-en-1-yl)ethyl)phenol partially is added to mixture and tempurature increased to 120-160 °C. Mixing process continues 20-60 minutes. Then, the mixture is washed with 10 % hydrochloric acid and distillated under low pressure. The solution is washed with ethil alcohol and its physicochemical properties determined.The effects of main factors that affects acylation reaction (tempurature, time, molar ratios of the initial components) to the solution extraction was analyzed. Results are given in fig. 1.



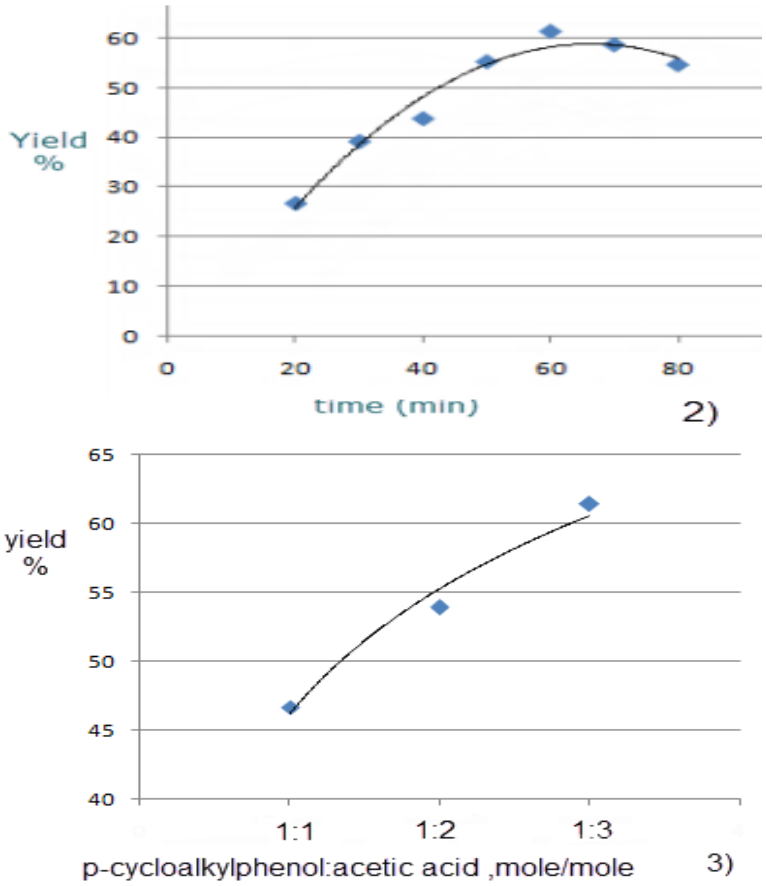


Fig.1. Curves of yields of 2-Hydroxy-5-(1-cyclohexene-3-il) ethyl) –acetophenone to 1) temperature 2) duration 3) mole ratio

As shown in the figure , at low tepuratures (120-130 °C) of acylation reactions, acetophenone yield is 46.7-49.2 % to cycloalkylphenol. The solution yield is 61,4 % when the reaction temperature is 160 °C; effetive results are not achieved at high tempuratures. As seen in fig. 1 (curve 2), the solution yield is 61,4 % in reaction zone where the duration of initial raw materials is at 1 hour. Effective results can not be obtained when the reaction time is increased or decreased. In the curve 3 the most effective mole ratio is 1:3 .Experiments show that, implementation of para-(1-(cyclohex-3-en-1-yl)ethyl)phenol to acetic acid with stoichiometric equation gives better results.

After distillation of the solution, IR and PMR spectrums were taken, then chemical structures and physicochemical properties were determined.

Table3.IQ-spectroscopic results of 2-Hydroxy-5-(1-cyclohexene-3-il) ethyl)–acetophenone

Absorption bands	Location in the structural formula
720 cm^{-1}	valent vibration of C–H bond in CH_2 group
825 cm^{-1}	1,2,4 subsituted benzene group
752, 790 cm^{-1}	C=C bond in cyclohexene
1015, 1110 cm^{-1} 3270 cm^{-1}	valent deformation vibration of phenol hydroxyl
1180, 1240 cm^{-1}	C-C bond in ArC(O)C- group
1455, 1370 cm^{-1} 2860, 2920, 2945 cm^{-1}	valent vibration of C–H bond in CH_3, CH_2 and CH group
1510 cm^{-1}	Benzene
1596, 1610 cm^{-1}	C=C
3025 cm^{-1}	C-H bond in -HC=CH- group
1735 cm^{-1}	C=O group

Physicochemical properties of synthesized -Hydroxy-5-(1-cyclohexene-3-il) ethyl) – acetophenone is given in table 4.

Table 4. Physicochemical properties of -Hydroxy-5-(1-cyclohexene-3-il) ethyl) –acetophenone

Structure formula	Empirical formula	Boiling point	n_D^{20}	ρ_4^{20}	Molar mass	Element substance, %			
						Calculated		Found	
						C	H	C	H
	$C_{16}H_{20}O_2$	171-173	1.5035	0.8900	244	78.7	8.2	78.3	8.6

CONCLUSION

The activation reaction of phenol with vinylcyclohexane and ortho-phosphoric acid was examined with presence zeolite catalyst-Y by intermittent facility. It was determined that, 4 hours at 100 °C, of initial components at 1:1 molar ratios and at 7 % catalyst (by taken phenol), the phenol solution (para-cyclohexene-3-il-ethyl) yield is 81.6 % and selectivity is 97.3 % according to the taken phenol. Hence, the acylation reactions of para-(cyclohexene-3-il-ethyl)-phenol with acetic acid by $ZnCl_2$ catalyst have been understood. As a result, the reaction at 160°C in 1 hour, the product 2-hydroxy-5-(cyclohexene-3-il-ethyl)-acetophenon yield is 61.4 % .

-Chemical structures and physicochemical properties of synthesized para-(cyclohexene-3-il-ethyl)-phenol and its derivative acetophenon were determined.

REFERENCES

1. Pat. 137651. Russia.1993
2. *Dubchenko C.I., Nikulina V.V., Terakh E.I. et al*..Synthesis and study of antiradical activities of substituted hydroxybenzylamines and their chlorohydrogenic salts. // Neftekhimiya, 2005,v. 45, p. 1-5 (in Russian).
3. *Markov A.F., Prosenko A.E., Shvarts Ya, Sh. Et al*.. Synthesis, toxic and gepaprotectorial properties of water-soluble derivatives on the basis of aminoalkylphenols. // Khim.-farm. zhurn. 40, № 4, p. 117-121 (in Russian).
4. Pat. 2174506. Russia.2006
5. Pat. 2233262. Russia.2004
6. Pat. 6417410. USA.2002
7. *Rasulov Ch. K., Nabiyev F.A., Babaeva R.K. et al*.. Synthesis of cycloalkylphenolic bases of Mannix. // Processes of petrochemistry and oil-refining. 2001, № 2, p. 37-40 (in Russian)
8. *Korenev D.K., Zavorotny V.A., Kelarev V.B*.. Searching for a catalyst for alkylation of phenol by olefins. Khimiya I tekhnologiya topliv I masel. 2003, № 1, p. 61-63 (in Russian).
9. *Rasulov Ch.K.,Azizov A.H., Zeynalova I.B. et al*.. Use of C_5 and C_8-C_9 fractions of gasoline pyrolyse for the synthesis of an antioxidate to oil VI Int. Conf. «Chemistry of oil and gas». Tomsk, 2006, 5-9 september, p. 455-456.