Synthesis of cyclohexyl esters for aliphatic saturated carboxylic acids with mono carboxyl group

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:Abstract

The use of the new and effective catalyst KY-2-8(H^+) in the esterification of the cyclohexanol with many aliphatic saturated carboxylic acids resulted in the formation of various cyclohexyl esters that can be used as basic fragrance substances. The optimal conditions to obtain the esters of cyclohexanol with carboxylic acids (C_1-C_5) were reported. The compounds identified by using IR spectra and NMR spectra, elements analysis occurred by C.H.N analysis .

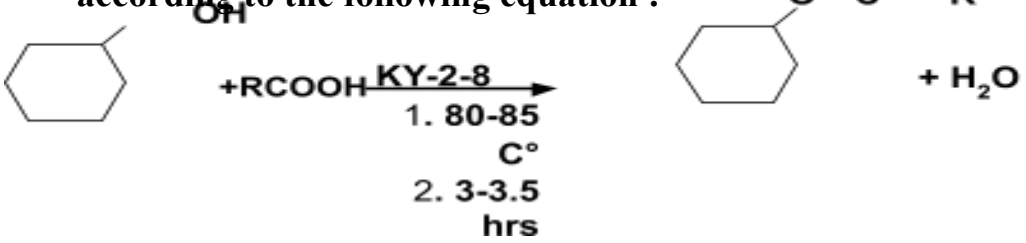
الخلاصة:

باستخدام العامل المساعد الجديد KY-2-8(H^+) ولأول مرة في عملية ألا سترة للسايكلوهكسانول مع العديد من الحوامض الاليفاتية المشبعة والتي بالنتيجة تم الحصول على عدد كبير من أسترات السايكلو هكسيل والتي يمكن استخدامها كمادة أساسية في مستحضرات العطور.تمت دراسة الظروف المثالية للحصول على أستر السايكلوهكسانول مع الحوامض الكاربوكسيلية المشبعة(C1-C5). شخصت المركبات بواسطة طيف الاشعة تحت الحمراء وطيف الاشعة فوق البنفسجية وتم التحليل بواسطة تقنية تحليل العناصر C.H.N .

:Introduction

The esterification of cyclohexanol in organic compounds is used successfully in the perfumes field and as a basic substance in other numerous preparations (1, 2). This group of cyclohexyl esters is also used as a component in the production of polymers. That gives the polymers an important physical and mechanical properties which improve their quality (3, 4). The cyclohexanol esters with the unsaturated acrylic acids are used successfully in the production of glue with very high properties , which is used in the medical field in the preparation of prosthetic teeth (5) , and in the colored ink of computer printer (6) . It's known that Sulpfonic acid is used as a catalyst in the esterification of cyclohexanol (7) .

The use of KY-2-8 as acidic catalyst in the esterification on showed an advantage by facilitating the production of cyclohexanol esters in heterogeneous phase to get these esters . The use of this catalyst facilitate the technology of esters production on the expense of getting rid of neutralization of acid and wash of the catalyst .The procedure of cyclohexanol esters in the presence of catalyst(H^+ from) KY-2-8 with aliphatic saturated carboxylic acid will occur according to the following equation :-



—When R = H—, CH_3—, C_2H_5—, C_3H_7—, C_4H_9—, C_5H_{11}

:Experimental part

The esterification procedure is employed by using the Din-stark device and cyclohexanol esterification is employed by using the acid according to the following procedure. (As example token cyclohexyl acetate) ,a mixture of 100 ml of cyclohexanol and 180 ml of acetic acid and 150 ml of Benzene , with 5 gm of catalyst ky-2-8 . Warming the mixture has been done by the device until 80-85 C° and at time of 3-3.5 h until of all water is removed at the same time 16.5 ml of water and 145ml of Benzene is accumulated . After cooling the ester compounds the catalyst was filtered and isolated Warming to 118-155 C° was done to get rid of the acid and alcohol which are not reacted , and separation of 132.4 ml from The reminant produce was done . After that the product is distilled under vacuumed pressure and we got 130ml of ester at 80 C° under vacuumed pressure of 40 mmHg . The study of physical-chemical properties is done which is compatible to that in the[7] . The cyclohexyl ester which is obtained from the use of cyclohexanol and the saturated carboxylic acid , which is considered as pure chemical compound , which is correspond to the substance prepared in [8] . The catalyst ky-2-8 is used for the first time .

:Result and Discussion

In order to produce the ideal conditions for the reaction , the catalyst which is used in the esterification reaction, and it is a cation exchange

K= Cation

Y= Universal

2-8 = Model

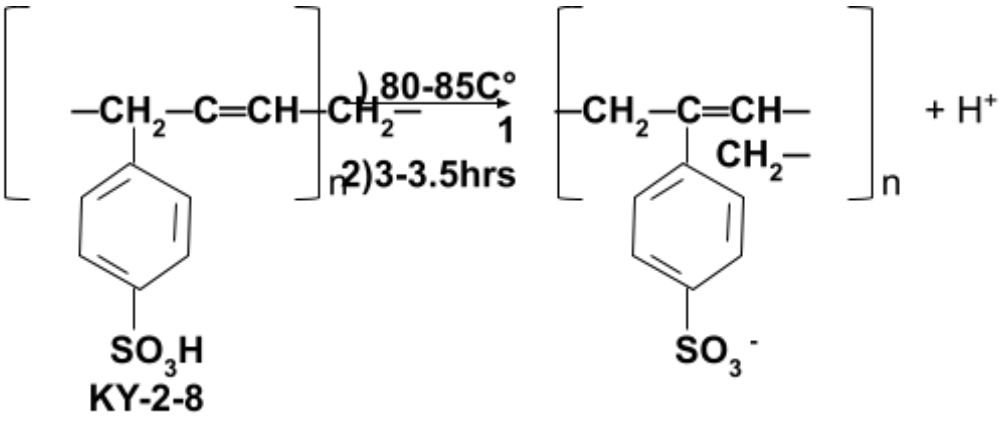
The molecular weight of the catalyst = 5000-8000

n= degree of polymerization

n=(5000-8000)/209=20-40 unit

209=M.wt for divinil enzyme sulfonic acid

The structure of the catalyst shows below:



Poly (P-bi vinyl benzene sulfonic acid)

The effect of the amount of the catalyst KY-2-8 , and the effect of mole ratio for the reactant materials are studied .

By using of the cyclohexanol and acetic acid as example , the study of the effect of quantity of catalyst КУ-2-8 (H^+) on the formation of cyclohexyl acetate is shown in table 1 .

. Table1: Effect of quantity of catalyst КУ-2-8 (H^+) on the product a-e

КУ-2-8	Products	
	Gram	%
3.0	69.0	48.6
3.5	73.8	52.0
4.0	83.3	58.7
4.5	85.7	60.4
5.0	93.1	65.6
5.5	89.5	63.0
6.0	85.0	60.0
6.5	82.3	58.0
7.0	78.9	55.6

a. Cyclohexanol: 100.0 ml
b. HOAc :60.0 ml
c.Temp: 80-85 Cº
d. Time : 3-3.5 hs
e. Solvent used : Benzene (150 ml)

From these results , the esters produced are depending on the amount of catalyst , so by increasing the amount of catalyst from (3%─5%).will leads to increase the amount of esters from (48,6─65,6%) and by increasing the percentage to 8% it will not give better outcome , so the ideal amount of catalyst is 5% is fixed this percentage for reactive substance (cyclohexanol and acetic acid) Table 2 . From the results of this table, the ideal mole ratio of cyclohexanol: acetic acid is (1:3) mole and by using this ratio the yield is 91.6% of the theoretical result of the reaction . By increasing the amount of acetic acid to 4.0 mole it will not increase the amount of esters produced . A study of prefect time for reaction has been done and the results was (3─3.5 h) which is enough time for the removal of calculated amount of water from the reaction.

Table 2: Effect of molar ratio of cyclohexanol(CHL) to acetic acid(HOAc) to . give cyclohexylacetate a-d

CHL:HOAC mole	HOAc ml	Products	
		Gram	%
1:1.5	80.0	104.1	73.3
1:2.0	120.0	111.1	80.4
1:2.5	150.0	115.0	84.0
1:3.0	180.0	130.0	91.6
1:3.5	210.0	130.2	91.7
1:4.0	240.0	130.2	91.7

a . CHL : 100.0 ml **d . Solvent used : Benzene (150 ml)**

b. KY2-8 : 5.0 gm

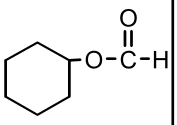
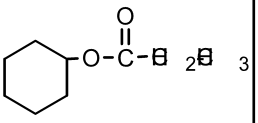
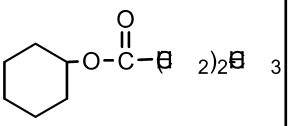
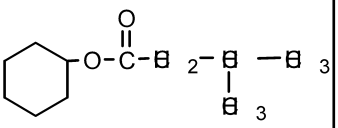
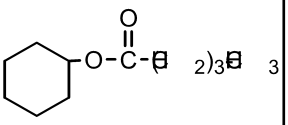
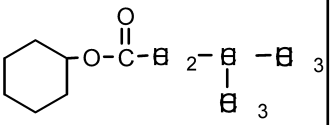
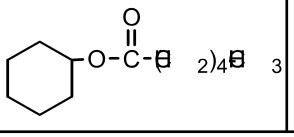
c . Temp : 80-85 Cº

Esterification reaction was done by the use of benzene as solvent and in the temperature of (80─85 C°) and these are the ideal conditions for the reaction of cyclohexyl acetate by esterification of the cyclohexanol with acetic acid in the presence of the catalyst KY-2-8 ($H^+$from).

Mole ratio cyclohexanol: acetic acid	1:3
.Quantity of KY-2-8 (H^+ from)	5% from cyclohexanol
. °Temperature	80─85 C
. Time	3─3.5 h

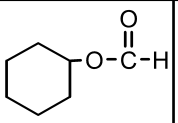
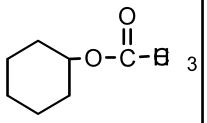
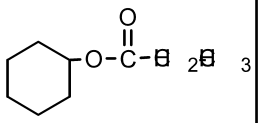
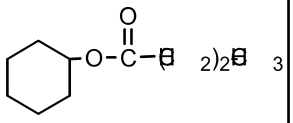
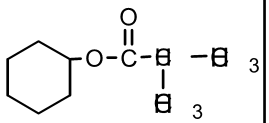
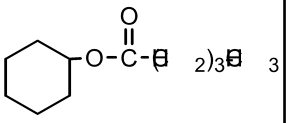
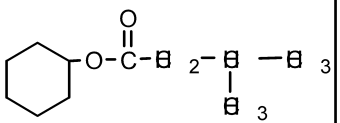
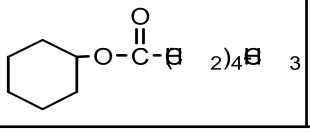
Under these conditions the result of cyclohexyl esters was 91.6%, and to obtain other types of esters under these conditions by the study of the esterification of cyclohexanol in comparison with another aliphatic acids and the results of this study is shown in table 3 .

Table 3. Condition of reaction and product a-d (Catalyst КУ-2-8 ($^+$H-form)-5% .mass

Reactants gram OK		Products		
Formula	gm	Structures	gm	%
HCOOH	138.0		117.7	92.0
C_2H_5-COOH	122.0		138.2	88.6
n-C_3H_7-COOH	262.0		143.6	84.5
i-C_3H_7COOH	262.0		140.9	81.0
n-C_4H_9COOH	306.0		146.3	79.5
i-C_4H_9COOH	306.0		136.9	74.4
n-C_5H_9COOH	348.0		154.4	78.0

The esters produced depend greatly on the structure of saturated acid that used . The results revealed that starting from formic acid till cabroic acid the resulted esters are decreased gradually from 92 to 74.4% with the exception of that , it appears that acid has iso group in comparison with normal acid will leads to the decrease of the esters to approximately 3.5-5.1% , and this occur due to the decrease in the acidity in the particles of acid with the iso group in comparison with that of normal. By the use of the chromatography of the purity of the prepared esters , it was determined that it was approximately 98.8-99.4%. The physiochemical properties of the prepared compound is shown in table 4 .

. Table 4. Physical-chemical properties and of the esters

Structure	Bp., ºC/mmHg	d_4^{20}	n_D^{20}	Found		Formula	theoretical	
				C	H		C	H
	46/40	0.9605	1.4506	65.61	9.31	$C_7H_{12}O_2$	65.62	9.37
	89/40	0.9560	1.4422	67.54	9.82	$C_8H_{14}O_2$	67.60	9.86
	105/40	0.9575	1.4435	69.10	10.29	$C_9H_{16}O_2$	69.19	10.32
	116/10	0.9418	1.4441	70.60	10.52	$C_{10}H_{18}O_2$	70.60	10.60
	110/10	0.9366	1.4390	70.55	10.49	$C_{10}H_{18}O_2$	70.60	10.60
	120/10	0.9338	1.4480	71.63	10.79	$C_{11}H_{20}O_2$	71.73	10.87
	56/1	0.9308	1.4401	71.64	10.86	$C_{11}H_{20}O_2$	71.73	10.87
	125/10	0.9233	1.4495	72.64	11.00	$C_{12}H_{22}O_2$	72.72	11.06

The prepared cyclohexyl ester is considered as colorless fluids and has odor similar to grass and plants . The cyclohexyl acetate esters is used as food flavors [7]. The chemical formula of the prepared esters were assigned by IR and PMR spectra table 3 .The IR spectra were done at (700 ─ 4000) cm^{-1} and the spectra showed highly absorption band at 1730,1740 cm^{-1} and 1100, 1180 cm^{-1} ,characterized for the esters group. The absorption at 1420 cm^{-1} and 2980 cm^{-1} belonged to the CH_2 group in Table 4 . In the NMRH spectra the chemical removal of CH_3 appears in the range of 1.11 ppm ,while the proton in the groups of (CH_2─COO^-) and (CH_2─O─CO) , appears at 2.28 ppm and 4.25 ppm . In the particles of cyclohexyl from the chemical shift of the proton appears in the group in the range of 8.20 ppm. The degree of purity for the esters prepared was determined by GLC .The analysis was done by chromatographic device LHM 8MD in Azerbaijan scientific academy. Length column is 2 m , and 10%of the liquid phase mass ethyleneglygolsuccenate on chrome layer is used . Temperature

of evaporator 250 C° and the column 150 C°, current detector 100 mA , the speed of transporting gas (Helium) 45ml /min. The spectrum of IR was done in UR-20 device by thin layer and spectrum NMR ^1H to the prepared substances was done in form of 10% solution of CCl_4 on the Tesla Bs-487and at 25 C°and at degree of 80 mhrtz, and as ideal measure internally HMDC with current measure of 0.05mdδ^+.

:References

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