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Synthesis 2-AlkylCyclohexanones by Free- Radical Addition of Cyclohexanone to Olefines

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الخلاصة :
تم في هذا البحث دراسة إضافة الجذر الحر للسايكلوهكسانون إلى عدة الكينات بوجود بيرسلفات الامونيوم كبادئ,وقد تم الحصول على مركبات 2-alkylcyklohexanones التي يمكن أن تستخدم لتحضير مركبات اروماتيه عطريه و يمكن استخدامها كماده أساس في تحضير مركبات عضويه مختلفة.

Abstract:
Free -radical addition of cyclohexanone to several alkenes studied in the presence of ammonium persulfate as initiator (In.) and as a result synthesized 2-alkylcyclohexanones that can be used as a source component of synthetic aromatic substances and use them as starting materials to produce various organic compounds.

Introduction:

First time Kharash showed that, by a free- radical addition cycloketones to unsaturated compounds and as a result generate the appropriate derivative ketones [1]. This idea was implemented and a number of scientists synthesized as a result of numerous derivatives cycloketones using as a baseline components of olefin hydrocarbons [2-4], vinyl ethers [5, 6], acrylonitrile [7], vinylketone [8], allyl compounds [9, 10]. The authors used organic peroxides and hydroperoxides as a initiator.

Modern chemistry cycloketones and its successful application in various industries as aromatic substances [11] to get cycloalcohol, plasticizers [12], super glues [13], it's need the development of environmentally sound and economically viable way to obtain 2-alkylcyclohexanones. In previous work[14] we have studied the reaction of accession to synthesis alkylcyclopentanones using inorganic compounds as initiator ammonium persulfate (AMP).

In this paper, continuing this trend, we have studied free-radical accession cyclohexanone to olefines .

Experimental Part:

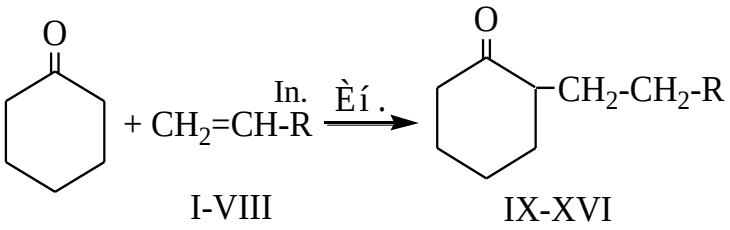
Reaction addition cyclohexanone to the olefines conducted in autoclave manufactured from stainless steel. In autoclave downloaded source component cyclohexanone and initiator AMP. In the hermetically closed autoclave filed through the connections of the container calculated the quantity of ethylene . Autoclave heated to 100 °C for 5 hours ,when the reaction was complete depending on the quantity of reacted ethylene, the pressure was reduce. The remaining unreacted ethylene removed through connections and liquid condensate separated and got 2-ethylcyclohexanone.The degree of purity alkylcyclohexanone determined to Gas Liquid Chromatography, LH-8MD. Terms of the analysis are: liquid phase 10% of the liquid phase mass ethylene glygol succenate on chrome layer, length columns 1.5 m, the temperature of the evaporator, columns and detector 200, 130 and 100 °C respectively, the speed of Helium-gas vehicle is 45 ml/ min., IR spectra of the device was removed at the UR-20 in a solvent CCl_4, and

the range of PMR ^1H on the device Tesla BS-487C.Used raw compounds were chemically fresh and clean, their physical and chemical constants coincided with literature data [15, 16].

The experiments were identified by the Azerbaijan scientific academy -Baku / Azerbaijan.

Results and Discussion:

AMP was used in this reaction as a initiator yielded tangible result of 2-alkylcyclohexanones[14]. It has been observed that cyclohexanone through selective radicals joined in the 2-position to olefins and formed with sufficiently high yield 2-alkylcyclohexanones:



I-VIII IX-XVI

R=H (I, IX), CH_3 (II, X), C_2H_5 (III, XI), n-C_3H_7- (IV, XII), CH_3-CH(-CH_3)- (V, XIII),

n-C_4H_9- (VI, XIV), n-C_5H_{11} (VII, XV), n-C_6H_{13}- (VIII, XVI)

Studied the influence of various factors on the exit 2-alkylcyclohexanones, for example, the reaction of cyclohexanone accession to ethylene in the presence of initiator AMP, found the optimal conditions as following:

molar ratio reactive components cyclohexanone: ethylene	2:1 (26 atm)
quantity of AMP (of the mass cyclohexanone)	0.5%
the temperature	100°C
the time of experience	5 hours

Material balance to get 2-ethylcyclohexanone as following:

I. Taken in reaction:

Cyclohexanone	176.0 g
Ethylene	28 g (22.4 l or 26 atm)
AMP	0.88 g
Total	204.88 g

After the reaction was finish, the pressure of no reactive of ethylene in the autoclave was 5.5 atm., and removed it through the valve, then we received **192.1** g from liquid alkyl-product, as tow sections:

First section: 61-62°C , 100.1 g. d_4^{20} 0.9474, n_D^{20} 1.4505.

This section consists of unreactive cyclohexanone, physical and chemical constants coincide with the literature data [14].

Second section: 113-114°C , 87.0 g, d_4^{20} 0.9125, n_D^{20}1.4506.

This section consists of a product 2-ethylcyclohexanone, physical and chemical constants coincide with the literature data [15].

Remaining	1.5 g
Loss	3.5 g
Total	199.1 g excluding unreactive ethylene

The selectivity of 2-ethylcyclohexanone was 75**%** mass of ethylene which_taken as reactant. Depended on hereinbefore developments, cyclohexanone added to another unsaturated aliphatic hydrocarbons (II-VIII).The result of these additions are shown in Table 1.

Table 1
Reaction Conditions of 2-alkylcyclohexanones From cyclohexanone-a olefines and in the presence of AMP.

Reactant			Conditions		Product	
Olefin in gm	cyclohexanone in gm	AMP, %	Temp. °C	hr	Structures	%
II – 42.0	176.0	0.88	100	5	X	71.0
III – 56.0	176.0	0.88	100	5	XI	70.5
IV – 70.0	176.0	0.88	100	5	XII	68.1
V – 70.0	176.0	0.88	100	5	XIII	61.3
VI – 84.0	176.0	0.88	100	5	XIV	60.0
VII – 98.0	176.0	0.88	100	5	XV	55.4
VIII – 110.0	176.0	0.88	100	5	XVI	54.0

As can be seen from the data obtained (Table 1) in the study of adherence cyclohexanone to olefins exit 2-alkylcyclohexanones reduced from 71.0 to 54.0%, Because the increase in the length of the chain Olefines ability of reaction reduced depending on the activity of π-bond. The degree of purity synthesized 2-alkylcyclohexanone determined chromatography analysis, it was 99.0-99.5%. They transparent liquids and physical, chemical properties are shown in Table2.

The structure of the synthesized alkylcyclohexanones proven I.R spectral method, in characteristic spectra reflected strong absorption bands in the 1720-1730 cm^{-1} proving the existence of carbonyl groups (C = O), 1380 cm^{-1} methyl group, 1175-1125, 2940-3010 CH- and CH_2-group in the chain and cycle.

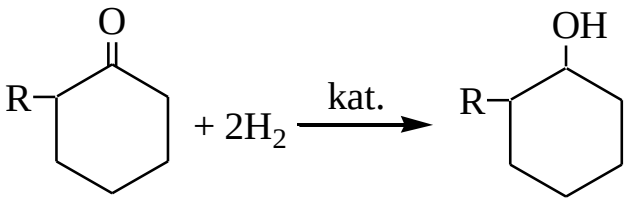
Synthetic alkylcyclohexanones also proved PMR ^{1} H spectral methods. Thus, shift 1.0 m.d. indicates the existence H-protons methylene group and shifts 1.45-2.35 m.d. in the side chain and methylene group in cyclohexane.

Table 2
Physical-chemical constants synthesized 2-alkylcyclohexanones

No. of compound	formula	Mol, mass	b.p. °C	d_4^{20}	n_D^{20}	Found % and (Theoretical) %	
						C	H
IX	$C_8H_{14}O$	126.2	113-114	0.9102	1.4506	76.0 (76.14)	11.18 (11.08)
X	$C_9H_{16}O$	140.23	84-85	0.9055	1.4527	77.0 (77.09)	11.39 (11.50)
XI	$C_{10}H_{18}O$	154.25	90-91	0.9015	1.4560	77.81 (77.87)	11.66 (11.76)
XII	$C_{11}H_{20}O$	168.28	109-110	0.9069	1.4580	78.35 (78.51)	11.88 (11.98)
XIII	$C_{11}H_{20}O$	168.28	105-106	0.8961	1.4587	78.46 (78.51)	11.80 (11.98)
XIV	$C_{12}H_{22}O$	182.31	120-122	0.8981	1.4600	79.0 (79.06)	12.02 (12.16)
XV	$C_{13}H_{24}O$	196.33	136-138	0.8900	1.4645	79.40 (79.53)	12.32 (12.32)
XVI	$C_{14}H_{26}O$	210.36	145-146	0.8890	1.4674	79.83 (79.94)	12.34 (12.46)

Fig. 1 shows I.R and PMR^{1}H spectra 2-n-hexylcyclohexanone.The most pleasant smell of synthesized alkylcyclohexanones has 2-n-hexylcyclohexanone and it can be used as a component for the preparation of perfume compositions.

The structure of the synthesized 2-alkylcyclohexanones also proved by reduce it to alcohol. So the pressure hydrogenation of 2-alkylcyclohexanones by hydrogen in the presence of Ni catalyst converted to alkylcyclohexanol.



R= àëêèëüíûå ðàäèêàëû
Free radical alkyl group

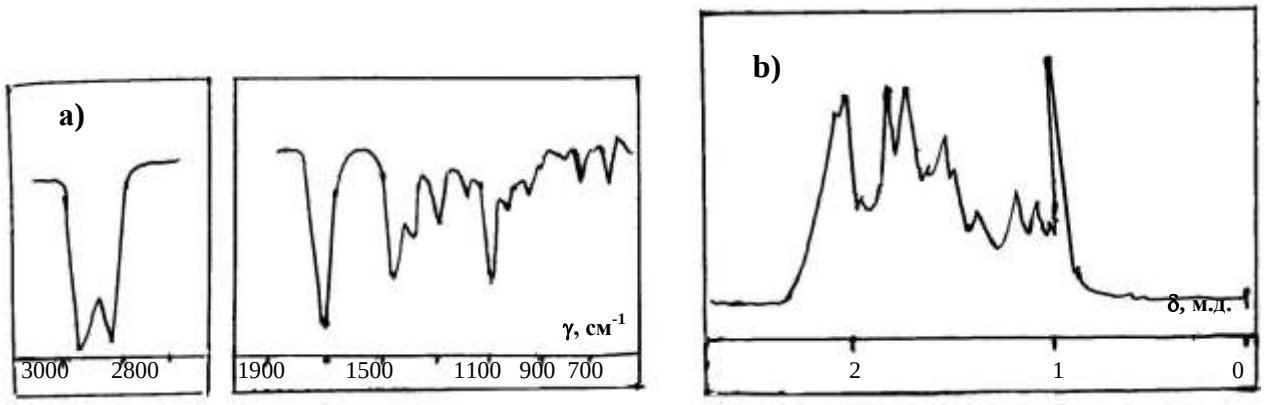
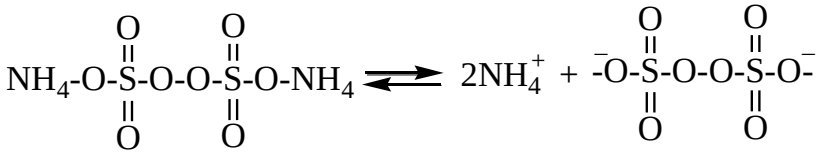
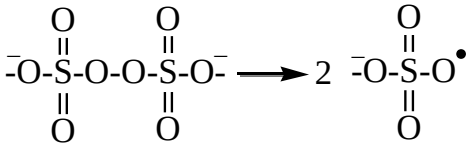
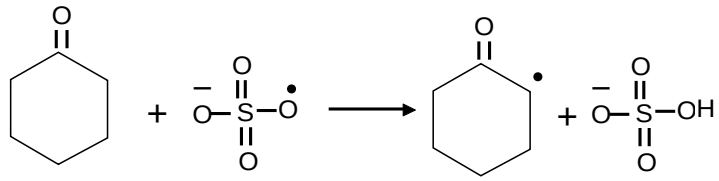


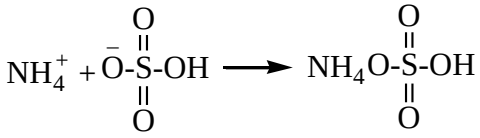
Fig. 1. IR (a) and the PMR ^{1}H (b) the range of 2-n-hexylcyclohexanone

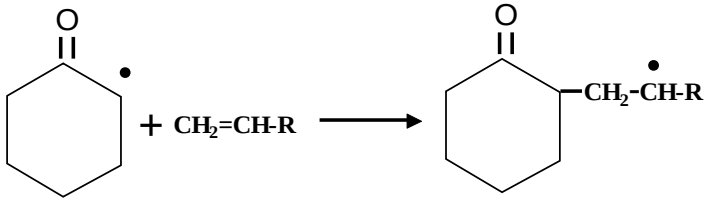
The Proposed Mechanism:

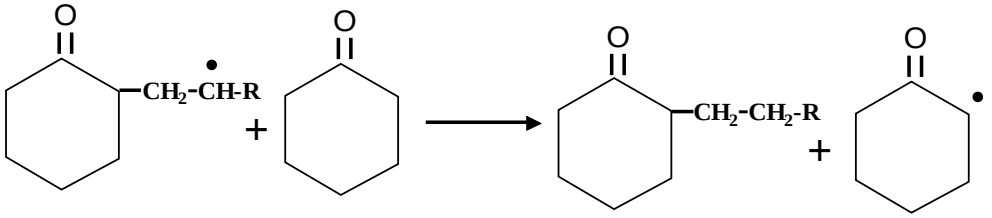












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