SYNTHESIS 2-ALKYLCYCLOPENTANONES BY ADDITION CYCLOPENTANONE TO OLEFINE

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Abstract:

The radical addition of cyclopentanone to ethylene in the presence of different initiators was studied. The most effective of these is ammonium persulfat(AMP), and with the use of ammonium persulfate were find the optimal conditions to get 2-ethylcyclopentanone. Studied the reaction of cyclopentanone with other olefins (C_3-C_5) and the synthesized 2-alkylcyclopentanone that can be used as a source component for the preparation of fragrance substances.

الخلاصة:

في هذا البحث تمت دراسة إضافة السايكلو بنتانون للاثيلين بواسطة الجذور الحرة وباستخدام مختلف المحفزات(البادئات).إن أكثر هذه البادئات فعالية هو بيركبريتات الامونيوم,وباستخدامه وجدت أفضل الظروف للحصول على 2-اثيل سايكلوبنتانون. تمت دراسة تفاعل السايكلوبنتانون مع اوليفينات مختلفة(C_3-C_5) لتخليق 2-الكيل سايكلوبنتانون الذي من الممكن استخدامه كمصدر أساسي لتحضير مستلزمات العطور.

Introduction:

Cyclopentanone (CPN) and its various derivatives alkyl-substitutions are valuable organic compounds and used successfully for the preparation of various fragrance substances. Some of them have physiological activity and thus used as insecticides in agriculture [1-3].

There are various ways of obtaining alkyl- and alkenyl -substitutions for cyclopentanone and their applications in the field of perfumery [4, 5], as well as unique in the food industry [6, 7].

Given the relevance of synthesis alkylcyclopentanone we have developed an effective way to get radical addition of cyclopentanone to olefinic hydrocarbons in the presence of initiator (In) .

Experimental part :

addition reaction of CPN to olefins in the presence of initiator (AMP) held in a steel rolling autoclave capacity of 1 lit. made of stainless steel. In Autoclave uploaded CPN and AMP, which dissolves in CPN and to mixture added ethylene, and container closed. Autoclave heated until the end of experience, then product has been separated from solution.

Using a baseline olefinic hydrocarbon (O.H.)propylene and Butylene-1 cooled by liquid nitrogen to determine the quantity of (O.H.).The composition and purity synthesized 2- alkylcyclopentanone defined by GLC analysis. Analysis conducted on the device LHM 8 MD-length columns 1,5 m, 10% of the liquid phase mass ethyleneglygolsuccenate on chrome layer. temperature evaporator 150 C°, current detector 100 mA , helium-gas vehicle, the speed is 45 ml/ min.

IR spectra of compounds in the device removed(identifecated by) UR-20, ^{1}H NMR spectra by spectrophotometer BS - 487 (CHR) at 80 MHz. An internal standard used GMDS, solvent CCl_4.

Initial compounds have the following physical and chemical constants:

Cyclopentanone: that boiling point. 130° C, d_4^{20} 0.9470, n_D^{20} 1.4366 [8].

ethylene: 1,260 kg/m^3, pyrolysis product, the purity is 99.0%.

propylene: 1,915 kg/m^3, pyrolysis product, the purity is 99.1%.

butylene: that boiling point. 6.3 C° d_4^{20}0.6675 ,n_D^{20} 1.3790 .

pentene-1: that boiling point. 30 C°, d_4^{20}0.6414, n_D^{20} 1.3715 .

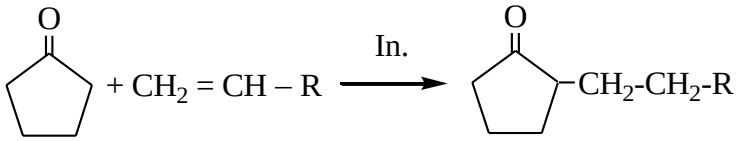
hexene-1: that boiling point. 63.5 C°, d_4^{20} 0.6731, n_D^{20}1.3824 .

Applied (In.)(benzoic anhydride, azobisizobutylnitril and ammonium persulfate) were chemically pure reagents and degradation their to radicals shown in [9].

Initial compounds ethylene and propylene are industrial products, and other olefins prepared by dehydration of saturated normal primary alcohols on the catalyst γ -Al_2O_3 and their physical and chemical constants coincided with literary data [10]. Synthetic 2- alkylcyclopentanones are transparent mobile liquids ,and from their products 2-butylcyclopentanone and 2-amylcyclopentanone have a pleasant smell a milt with a touch of greenery and flowers, which are of interest in synthetic fragrant substances.

Results and Discussions:

Reaction to join cyclopentanone to olefinic hydrocarbons in the presence of initiator was happen by radical mechanism anti- Markovnikovs rule to form 2-alkylcyclopentanones:



R = H; CH_3-; CH_3-CH_2-; CH_3-CH_2-CH_2-; CH_3-CH_2-CH_2-CH_2-

In order to select good initiator to get alkylcyclopentanones was study the reaction addition of cyclopentanone to ethylene (ET) in the presence of organic and inorganic initiators, the results of which are shown in Table 1.

Table 1

The effect of initiators on the synthesis of 2- ethylcyclopentanones by reaction addition of cyclopentanone to ethylene (In-0.1 wt%. from CPN)

	reactants		conditions		2- ethylcyclopentanone	
In. structures and nomenclature	CPN in gm	Ethylene in atm	temperature °C	Time in hr.	gm	%
$(CH_3)_3COOC(CH_3)_3$ tert-butanoic anhydride	84	25	140	3	37,5	33,5
$(CH_3)_3$-COO-C(=O)-C$_6$H$_5$ tert-butylperbenzoate	84	25	120	3	34,7	31,0
C$_6$H$_5$-C(=O)-O-O-C(=O)-C$_6$H$_5$ benzoic anhydride	84	25	100	3	31,8	28,4
$(CH_3)_2$-C(CN)-N=N-C(CN)-$(CH_3)_2$ azobisizobutylnitril	84	25	80	3	45,9	41,0
NH_4-O-S(=O)$_2$-O-O-S(=O)$_2$-O-NH_4 persulfat ammonium	84	25	90	3	54,2	48,4
$(CH_3)_3$-COOH tert-butanoic acid	84	25	70	3	25,1	22,4

Of the results shows that the best(In.) to get of 2- ethylcyclopentanone is persulfat ammonium (AMP), where gives (CPN) in 48.4% yield of the theoretical. Therefore, in order to find the

optimum conditions for synthesis 2- ethylcyclopentanone we used (In , AMP) and with the participation studied the effect of temperature, molar ratio (CPN) to (ET) and duration of experience. The results are shown in Fig. 1.

Temperatures varied in the range of 70 to 100 C° (Fig. 1, curve 1) and found that the yield of ethylcyclopentanone increased from 16.5% to 50%,at (70 -90) C° while further enhancing its 100 C° withdrawal reduced to 43.0%.

When we found the optimal temperature (90 C°) ,the influence molar ratio CPN to ET were study, the results are shown in Fig. 1, curve 2.

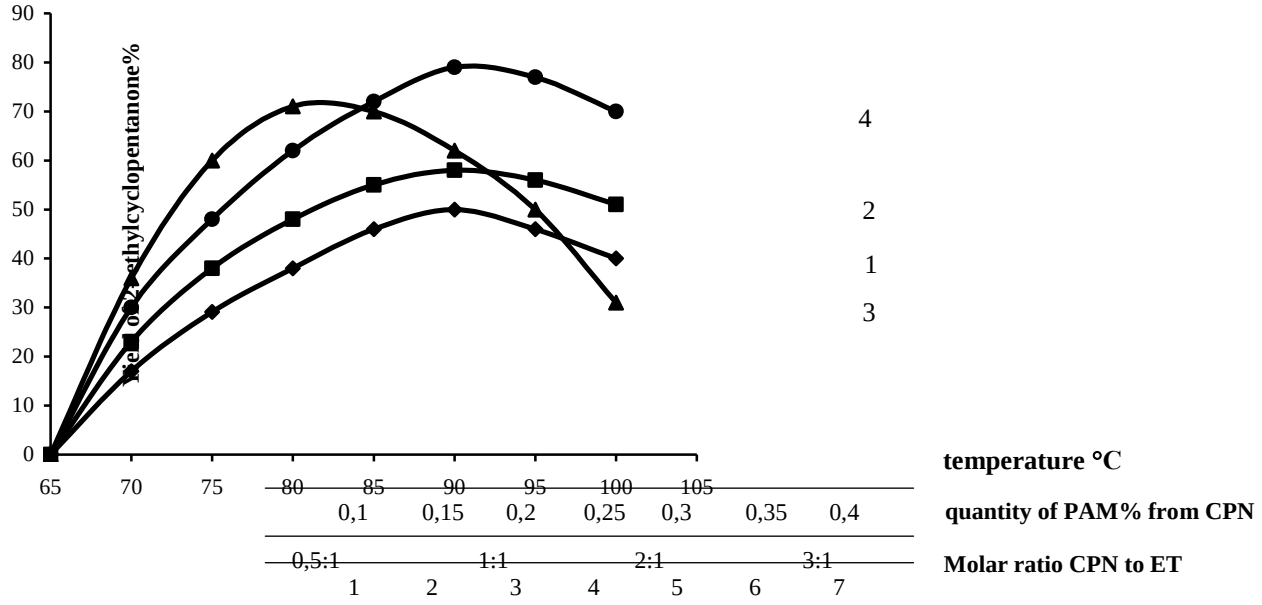


Fig. 1. Effect of temperature (1), the molar ratio of CPN to ET (2), Quantity of initiator AMP (3) the duration of experience (4) to give 2-alkylcyclopentanone.

The statistics showed that the molar ratio of ET-CPN 2:1 increases
2- ethylcyclopentanone to 58.6%, and a further increase their ratio to 3:1 mole, in contrast, affects the main product decrease to 51.0%.

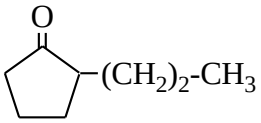
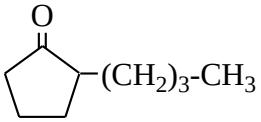
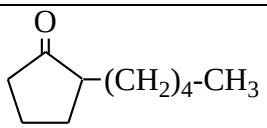
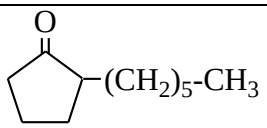
As for the impact of initiator - ammonium persulfate to product, the amount 0.2% of the mass CPN led to increase 2- ethylcyclopentanone from 44,1 to 72,0%, and a further increase in their numbers has led to a strong reduction in output target product to 32.5%.It seems that high levels of initiator causes recombination intermediate radicals in the system broken a chain of 2- ethylcyclopentanone (Fig. 1, curve 3).

In examining the effects of duration of the reaction (Fig. 1, curve 4) revealed that up to 5 hours out 2- ethylcyclopentanone reaches maximum 80.0%, but a further increase in contact time does not lead to a positive result trust product ketone. Found optimal synthesis of 2- ethylcyclopentanone accession to the ET in the presence of initiator AMP are:

temperature 90 C°
mol. Ratio CPN: 2:1 ET (25 atm)
In. amount AMP 0.2% of the mass CPN
duration experience 5 hrs
with these conditions, 2- ethylcyclopentanone is 80.0%.
When shown a studied addition CPN to other olefinic hydrocarbons:

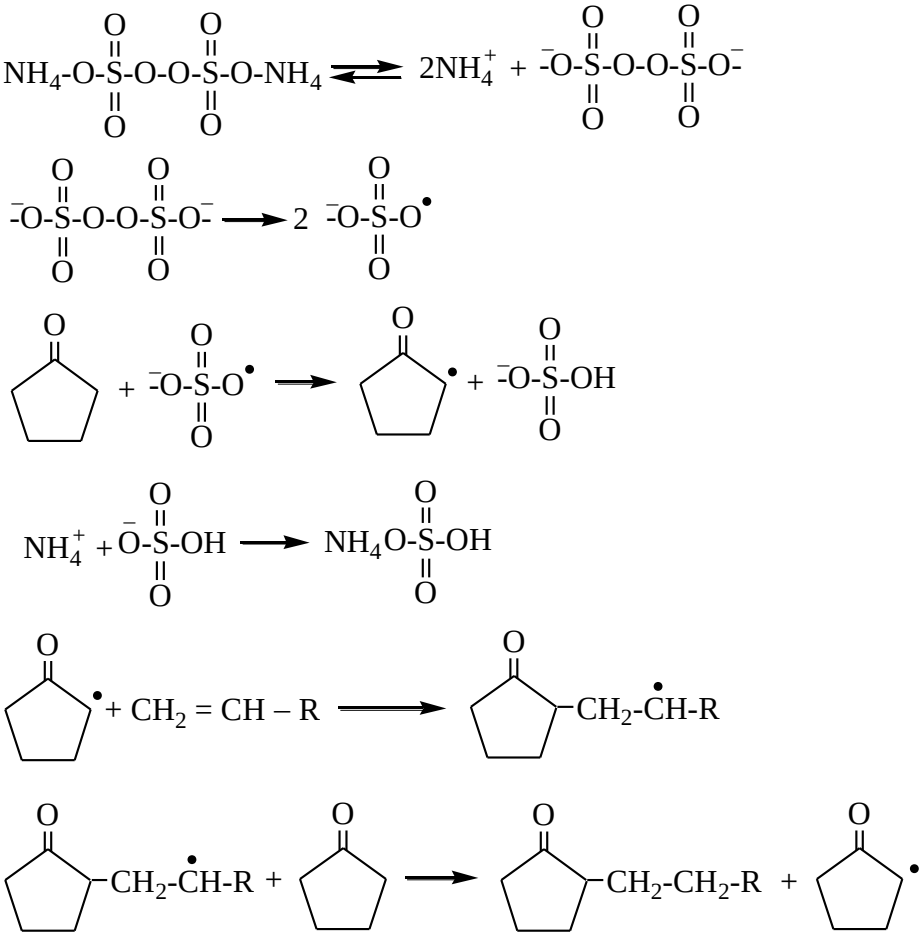
propane, butene-1, pentene-1 and hexene-1.
Table 2 shows the results of the data.

Table 2
CPN - a radical addition to the olefinic hydrocarbons in the presence of AMP

reactant			conditions		product	
CPN in gm	Olefin in gm	AMP, %	°C	hr	structures	%
168	CH_2=CH-CH_3 42	0,2	90	5		78,1
168	CH_2=CH-CH_2-CH_3 56	0,2	90	5		74,5
168	CH_2=CH-$(CH_2)_2$-CH_3 70	0,2	90	5		70,0
168	CH_2=CH-$(CH_2)_3$-CH_3 84	0,2	90	5		68,2

From the experimental data (Table 2) shows that the increase in mol. Mass olefinic hydrocarbons from the ET to hexene-1 causes reduced products from 80 to 68.2%. Apparently length alkyl-radicals in the molecule baseline olefinic hydrocarbons affects the activity π-bond in their molecules. Given the collapse of the initiator persulfat ammonium offer the following mechanism of synthesis 2- ethylcyclopentanone:

The Proposed Mechanism



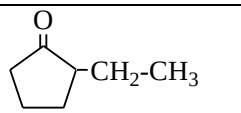
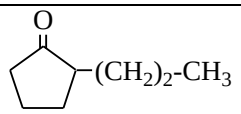
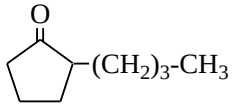
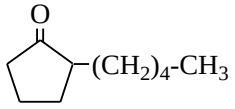
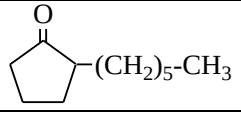
The degree of purity synthesized alkyl-CPN defined by chromatographic analysis, and found that they are pure chemical compounds (99,1-99,5%).

Table 3 shows the physical chemistry properties of synthetic 2-alkylcyclopentanone.

The structure of synthetic 2- alkylcyclopentanone proven IR spectral method. All spectra of synthesized compounds are strong intense absorption bands in the 1720-1725 cm^{-1}, indicating that the molecule carbonyl (> C = O) and 1380 cm^{-1} methyl groups ($-CH_3$). Flat deformation fluctuations 1175-1125 cm^{-1} proved Methen (-CH), and 2940-2015 cm^{-1} methylene ($-CH_2$) group in a cycle; 710-720 cm^{-1} show methylene (CH_2) groups in the chain.

In study of 2- alkylcyclopentanone by PMR spectral methods revealed that chemical shift Changes evident methyl 0,9 m.d. and alkyl-substitutions 1,4-2,2 m. d. Fig. 2 shows IR and PMR spectra ^1H for 2- alkylcyclopentanone.

Table3
Physical and chemical constants and the element of the synthesized 2- alkylcyclopentanone

structures	Mol, mass	Temp. °C	20 4	20 d	Found %		formula	theoretical	
					C	H		C	H
	112,17	70	0,9068	1,4420	74,81	10,69	$C_7H_{12}O$	74,95	10,78
	126,20	100-101	0,8978	1,4461	76,04	11,07	$C_8H_{14}O$	76,14	11,18
	140,22	113-114	0,8959	1,4485	76,91	11,39	$C_9H_{16}O$	77,09	11,50
	154,25	133-134	0,8950	1,4516	77,68	11,66	$C_{10}H_{18}O$	77,87	11,76
	168,28	155-156	0,8925	1,4530	78,39	11,86	$C_{11}H_{20}O$	78,51	11,98

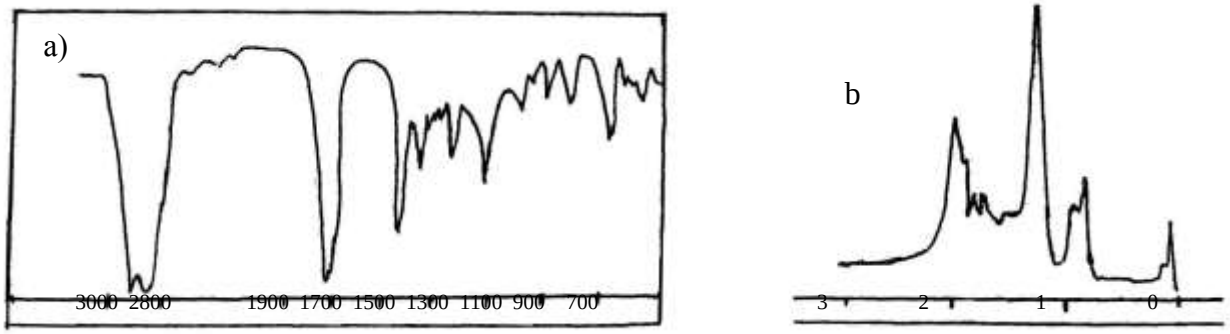


Fig**. 2. IR spectrum (a) and ^{1} H PMR spectrum (b) for 2- alkylcyclopentanone**

References:

1. Myammyadov MK *Yatirli maddyalyar. Baki: Elm*. 2006. p .303.
2. Bratus I. N. *Chemistry fragrant substances*. M: Agropromizdat. 1992. p .420.
3.Elizarov A. N. *Mall Chemistry cyclopentanones*. M: Science. 1966. p .281.
4. Nikishin G. I., Somov G.V / *JOC*. 1967. T.3. No. 2. p.299.
5. A. C. No. 505196. 1974 (USSR).
6. Heyfits L. A., Dashunin V.M Aroma substances and other products for perfumes. *M: Chemistry*. 1994. p. 235.
7. Abbasov M. F. / *Azerb.chem. J*. 2004. No. 3. S.105-108.
8. Fluka. *Chemika-Biochemica* / 1993-94. p.413.
9. Workshop on Polymer Chemistry. *M: Chemistry*. 1990. p. 300.
10. Gornowski I. T.,. Nazarenko U.P., Nekryach E. F. *Digest chemist. Microsoft in: Naukova accord*. 1974. p 991.