



Science

HOMOGENEOUS VINYLATION OF 2-HYDROXY-2-PHENYLETHANICAL ACID

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Abstract

Homogeneous-catalytical vinylation of 2-hydroxy-2-phenylethanical acid was carried out. Influence of catalylists nature, temperature and duration reaction on yield of synthesized vinyl ester has been investigated.

basis of natural raw materials. Based on vinyl esters of carboxylic acids, their polymers and copolymers with unsaturated compounds of the ethylene series, emulsifiers for emulsion paints have been obtained; compounds that improve the viscosity of lubricating oils and are used as crosslinking agents in the rubber industry. Synthesis of vinyl esters based on monobasic aliphatic acids has been studied by the example of acetic acid by many researchers. In this respect, the aromatic carboxylic acids remain unexplored.

Goal: Synthesis of vinyl ester of mandelic acid by it's reaction with acetylene in the presence of heterogeneous catalysts, investigation of the influence of the nature of catalysts and the reaction temperature on the yield of obtained product.

Methodology: Catalytic systems based on $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ or zinc salt of mandelic acid with dimethylsulfoxide were prepared and heterogeneous catalytic vinylation of mandelic acid with acetylene was carried out and it's vinyl ether was obtained.

Scientific Novelty. The synthesis of vinyl ester of mandelic acid with it's reactions with acetylene using the catalytic systems $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ -DMSO and $(\text{C}_6\text{H}_5\text{CH}(\text{OH})\text{COO})_2\text{Zn}$ -DMSO was carried out.

Obtained Data: The vinyl ester of mandelic acid was synthesized by it's vinylation in stationary heterogeneous conditions. The influence of the nature of the catalyst ($\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$, $(\text{C}_6\text{H}_5\text{CH}(\text{OH})\text{COO})_2\text{Zn}$), temperature and duration of the reaction on the yield of the product was investigated.

Features:

- vinylation of hydroxy carboxylic acid was investigated;
- the catalytic systems $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ -DMSO and $(\text{C}_6\text{H}_5\text{CH}(\text{OH})\text{COO})_2\text{Zn}$ -DMSO are used;
- factors influencing the yield of vinyl ester of mindalic acid and optimal conditions of it's synthesis were found.

Keywords: Mindalic Acid; Acetylene; Heterogeneous Catalysis; Influencing Factors on Product Yield; Catalysts: $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ and $(\text{C}_6\text{H}_5\text{CH}(\text{OH})\text{COO})_2\text{Zn}$.

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1. Introduction

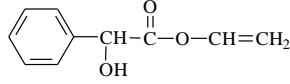
Vinyl esters are important compounds because owing to presence in their molecules of double bond and ether group on their base different chemical transformations can be carried out. Such compounds are wide used at obtain dyes, at production of monomer for obtain different polymers. On the base of vinyl esters of carbonic acids, their polymers and copolymers were obtained also compounds, on their base containing double bond were used for obtain which were used at obtain of different emulgators and dyes; compounds improving viscosity of lubricates and cross-linking agents for rubber-technical industry also have been obtained. At present time the high demands to polymeric materials is caused by concurration what has carried out to increasing of quality of products and their cost. Also using of natural compounds in this range also is very important [1,2]. 2-Hydroxy-2-phenylethanical acid (mandelic acid) is a natural compound which is entered in composition of mandale. On its base antiseptics using in medicine as initial compounds for obtain antibiotics were obtained. Its ammonium and calcium salts are used as urinegonic substances in urology. Also it is used as analytical reagent for determination of ions of Ti, Fe, Al, Cr, V and for deviation of Zn from Mo [3-5]. Acid properties of investigated acid are hier in comparison with acetic acid what is influenced on its biological activity and limited spheres of its using. By this reason decreasing of its acid properties has allowed to increase biological activity of mandelic acid. According to above mentioned in this work homogeneous-catalytical vinylation of mandelic acid was carried out in solution of dimethylsulfoxide (DMSO) in the presence of catalysts-zinc salt of mandelic acid and its composition with $AlCl_3 \cdot 6H_2O$ at temperature 80-140 °C. Acetylen has been past through mixture mandelic acid-DMSO-catalyst with rate 0,1 mole/h. At this vinyl ester of mandelic acid was formed as main product according to following scheme:



Obtained ester is a new organical compound unknown in literature and its some physico-chemical properties are presented in table 1.

Table 1: Some physico-chemical properties of vinyl ester mandelic acid

Structural formule	Yield, %	Data of IR-spectrometry		Data of PMR-spectrometry	
		characteristical groups	value of, sm^{-1}	characteristical groups	value of, <i>m.d.</i>
	84,4	OH	3430,28	OH	2,0
		CH- (OH)	2917,35		
		C=O	1712,09	=CH ₂	4,85-4,55

	CH=CH ₂	1663,14	=CH	7,25
	(Ar) =CH	3003,11	-CH	5,34
	C-O-C (СИММ. ВАЛЕНТ)	1025	C ₆ H ₅	7,38- 7,36

Temperature has influenced in great degree on carrying out of investigated catalytical reaction. By this reason the influence of this parameter on the vinylation of mandelic acid by acetylene in the presense of it's Zn salt as catalyst has been investigated and obtained results are presented in table 2.

Table 2: Influence of temperature on vinylation of mandelic acid in the presence of it's zink salt (10%) as catalyst and rate of acetylene past through 0,1 mole/h

№	Temperature of reaction, °C	Yield of vinyl ester, %
1	80	45,8
2	90	49,4
3	100	56,6
4	110	63,2
5	120	65,9
6	130	61,5
7	140	53,4

As shown from obtained results the great influence on vinylation of mandelic acid by acetylene the temperature has rendered. In investigated range of temperature 80-140 °C it's vinyl ester was formed yield of wich has changed with temperature: increasing of temperature from 80 to 120 °C caused to increasing of product yield from 45,8 to 65,9% and following increasing of temperature befor 130 °C has caused it's decreasing and at this also decomposition of DMSO with formation of sulfur-containing compounds with following formation cross-linking oligomeric products was observed. For vinylation of mandelic acid by acetylene the optimal temperature was 120°C and at this yield of forming vinyl ester was equaled 65,9% and correspondenly following investigations were carried out namely at this temperature. In table 3 results by influence of temperature on vinylation of mandelic acid in the presence of it's zink salt treatment by AlCl₃·6H₂O (10%) as catalyst are presented.

Table 3: Influence of temperature on vinylation of mandelic acid in the presence of above-mentioned catalyst (time-2 h; rate of acetylene past through 0,1 mole/h)

№	Temperature of reaction, °C	Yield of synthesised vinyl ester, %
1	80	65,3
2	90	68,7
3	100	69,6
4	110	73,9
5	120	79,8
6	130	67,5
7	140	63,4

From obtained results it is shown that in presence of elaborated catalyst in temperature range 80-120 °C yield of forming vinyl ester of mandelic acid has increased from 65,3 to 79,8 and at this introduction of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ in composition of catalyst has increased its catalytical activity.

It is known that in stationary state on the rate of chemical reaction and yield of product the duration of reaction (time) has a very important role. By this reason the influence of this factor on the formation of the base product-vinyl ester of mandelic acid was investigated and obtained results are presented in table 4.

Table 4: Influence of process duration on vinylation of mandelic acid in the presence of its zinc salt as catalyst, rate of feeding of acetylene 0,1 mole/h, temperature 120 °C

Duration of reaction, h	Yield of vinyl ester of mandelic acid, %
1	48,7
2	65,9
3	69,7
4	71,1
5	69,8
6	67,2

It is shown that yield of obtained vinyl ester was increased from 48,7 to 71,1 % correspondingly at increasing time of reaction from 1,0 to 4,0 h, but at following increasing of duration of reaction yield of product has decreased on 1,3-2,6 % that is optimal duration of carrying out of investigated reaction was equaled 4 h.

According to data of chromatographical analysis at time of reaction 3 h beside of base product also mandelic acid didn't entered in reaction was observed; at time of reaction more then 4h also formation of rubber-similar compounds owing to oligomerisation and polymerization of obtained vinyl ester and its cross-linking by H_2S forming owing decomposition of solvent DMSO was observed.

At investigation of vinylation of mandelic acid in the presence of its salt + $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ (10%) as catalyst have been obtained results, presented in table 5.

Table 5: Influence of duration of vinylation mandelic acid in the presence of above mentioned mixing catalyst at temperature 120 °C and rate feeding of acetylene 0,1 mole/h

Duration of reaction, h	Yield of vinyl ester of mandelic acid, %
1	56,5
2	79,8
3	83,2
4	84,4
5	82,9
6	81,1

From data of table 5 it is shown that introduction in composition of catalyst ingredient $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ has increased its activity owing to fact that it implements role of promotor. In the presence of this catalyst yield of vinyl ester during 1-4h was increased from 56,5 to 84,4%.

2. Conclusions

It was shown that at vinylation of mandelic acid by acetylene in the presence of catalyst $(C_6H_5CH(OH)COO)_2Zn$ the it's vinyl ester has been formed.

It was determined that introduction in composition of catalyst ingredient $AlCl_3 \cdot 6H_2O$ (10%) as promotor has caused increasing of yield of forming vinyl ester.

It was determined that temperature, duration of reaction and nature of used catalyst have great influence degree on the yield of vinyl ester of mandelic acid.

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