CHEMISTRY & CHEMICAL TECHNOLOGY

Vol. 5, No. 4, 2011 Chemistry

Maria Fedevych

a-UNSATURATED ACIDS IN DIELS-ALDER REACTION

Lviv Polytechnic National University,
12, St. Bandera str., 79013 Lviv, Ukraine

Received: June 03, 2011 / Revised: August 28, 2011 / Accepted: September 30, 2011

Abstract. The effect of reagents molar ratio and temperature, the amount of toluene as solvent and pyrogallol as inhibitor on the yield of alkylcyclohexene acids has been established at their production *via* Diels-Alder reaction using 2,3-dimethylbuta-1,3-diene and alkylacrylic acids. The structure and physico-chemical characteristics of the synthesized compounds have been determined.

Keywords: 2,3-dimethylbuta-1,3-diene, α-acrylic acids, Diels-Alder reaction, 3,4-dimethyl-1-alkylcyclohexenic acids.

1. Introduction

Cyclohexenic acids are widely used for the synthesis of a bulk of reactive derivatives – esters, amides, nitriles and others, as well as for the production of polyperoxypolyazocompounds which are initiators with an increased initiating action in the graft-copolymerization processes [1].

Studying the behavior of α-unsaturated aldehydes in the Diels-Alder reaction (both in the dimerization reaction and condensation reaction with different dienophiles, namely with α-alkylacrylic acids) it was established that the cyclohexenepyranic acid is formed but the lactonization takes place during its extraction.

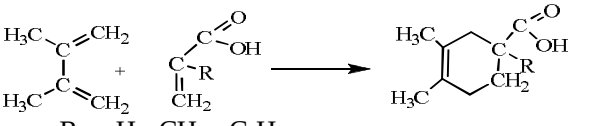
In this work the condensation reaction of α-unsaturated acids with 2,3-dimethylbuta-1,3-diene has been investigated. The mentioned compounds are industrially available and more reactive than alkylacroleins. The aim was to obtain 3,4-dimethyl-1-alkylcyclohexenic acids (3,4-DMACHA).

The information about this class of valuable products is limited by the first two terms of homologous series of cyclohexenic acids: 3,4-dimethylcyclohexen-carbonic acid (3,3-DMCHA) [2] and 1,3,4-trimethylcyclohexencarbonic acid (1,3,4-TMCHA) [3].

To extend the knowledge concerning the usage of the Diels-Alder reaction which is very important as one of the methods of carbo- and heterocyclic structures construction and to enlarge the range of compounds of cyclohexenic row the effect of conditions on the reaction proceeding and acids yield at the interaction between α-alkylacrylic acids and 2,3-dimethylbuta-1,3-diene (DMB) was studied.

2. Experimental

3,4-Dimethyl-1-alkylcyclohex-3-ene-1-carbonic acids were synthesized *via* cycloaddition reaction of 2,3-dimethylbuta-1,3-diene to α-unsaturated acids by the scheme:



R = -H, -CH_3, -C_2H_5.

2,3-Dimethylbuta-1,3-diene was synthesized *via* catalytic dehydration of 2,3-dimethyl-2,3-butanediol according to the procedure described in [4].

Acrylic (AA) and methacrylic (MAA) acids were purified by distillation. α-Ethylacrylic acid (EAA) was synthesized *via* oxidation of α-ethylacrolein according to the procedure described in [5].

Toluene, DMB stabilized by pyrogallol and α-unsaturated acid were loaded into thermostatically controlled autoclave which was blown with nitrogen. The synthesis was carried out for 4–5 h within the range of 388–423 K. Then toluene was distilled and 3,4-DMACHA was rectified under vacuum.

For quantitative determination of unsaturated C=C bonds the Liukas-Presmann modified method was used [6]. The acid number was determined using titrimetric method [7]. The acid structure was proved by chemical, elemental and spectral analyses.

The synthesized alkylcyclohexenic acids are white crystalline compounds with the following characteristics:

3,4-dimethylcyclohexen carbonic acid (3,4-DMCHA), $C_9H_{14}O_2$, m.p. 354–354.5 K, b.p. 387 K/2 mm Hg. Found (%): C 69.68, H 9.03. Calc. (%) C 70.04, H 9.08. Yield 95 %.

1,3,4-trimethylcyclohexen carbonic acid (1,3,4-TMCHA), $C_{10}H_{16}O_2$, m.p. 329–329.5 K, b.p. 389 K/2 mm Hg. Found (%): C 70.98, H 9.46. Calc. (%) C 71.34, H 9.51. Yield 88 %.

3,4-dimethyl-1-ethylcyclohexen carbonic acid (3,4-DM-1-ECHA), $C_{11}H_{18}O_2$, m.p. 322–323 K, b.p. 393 K/2 mm Hg. Found (%): C 72.08, H 9.83. Calc. (%) C 72.45, H 9.88. Yield 82 %.

The acids structure was confirmed by the spectral analysis. NMR ^{1}H spectrum was recorded using Bruker AM-300 (300 MHz) spectrometer in $CDCl_3$, TMS as an internal standard.

The spectrum has signals of 0.90, 1.52, 1.72, 1.82, 1.82, 1.91, 1.97, 2.01, 2.02, 2.27 and 12.08 ppm. The protons of the acid groups are registered at 12.08 ppm as a singlet. Six protons of cyclohexenic fragment show four doublet signals at 1.72, 1.91, 1.97, 2.01, 2.02 and 2.27 ppm. Methyl groups in the cycle at 3,4 positions resonate as a singlet at 1.82, 1.82 ppm. Ethyl group at the first position resonates as a triplet at 0.90 ppm and as a multiplet at 1.52 ppm.

3. Results and Discussion

The effect of reagents ratio, solvent and inhibitor amounts and temperature on the yield of the main products has been studied.

At the interaction between DMB and AA without the solvent the yield of 3,4-DMCHA is less by 10 % compared with that in the toluene medium (Fig. 1).

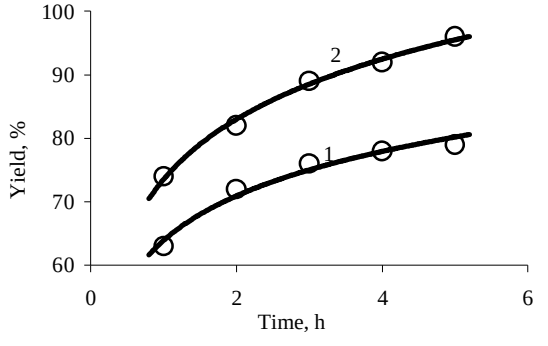


Fig. 1. Dependence of 3,4-DMCHA yield upon the medium at the interaction between DMB and AA: without the solvent (1) and in toluene (2). Temperature is 388 K, molar ratio DMB: AA = 1.2:1

It is obvious that dimerization, polymerization and other side reactions take place apart from dienic condensation under mentioned conditions. The application of inhibitors, the decrease of cycloaddition temperature and selection of corresponding solvents sometimes allow to restrain the side reactions and increase the yield of the main product.

It was established that for the condensation reaction of DMB with acrylic acids toluene is the most acceptable solvent. The effect of toluene on the process parameters within the range of volumetric ratios reagents : toluene = = 1:1–3 was investigated. The double excess of toluene was found to be the optimum one (Fig. 2).

Changing the inhibitor amount from 0.9 to 1.2 % we found that 1 mas % of pyrogallol (to calculate from the reagents mass) is enough to prevent polymerization (Fig. 3).

Changing the ratio DMB : unsaturated acid was found that 3,4-DMACHA high yields may be achieved at 1.2-multiple molar excess of DMB. The further increase of DMB amount does not increase the yield of the main product (Fig. 4).

At the interaction between DMB and AA with the increase of temperature from 368 to 388 K the reaction rate increases and at 388 K the process comes to the end after 4-5 h. 3,4-DMCHA yield is 95 % at 388 K.

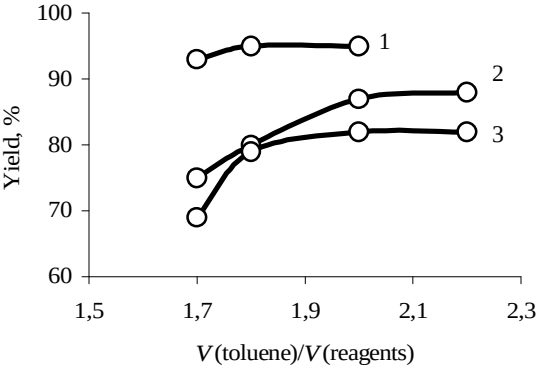


Fig. 2. Dependence of 3,4-DMACHA upon regents : toluene ratio: AA (1); MAA (2) and EAA (3)

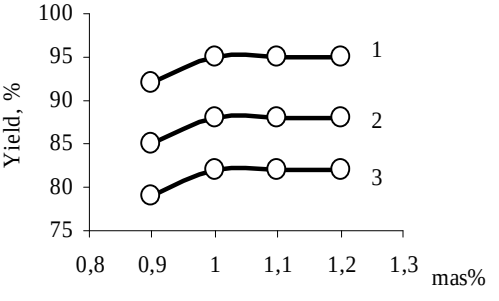


Fig. 3. Dependence of 3,4-DMACHA yield upon pyrogallol amount: AA (1); MAA (2) and EAA (3)

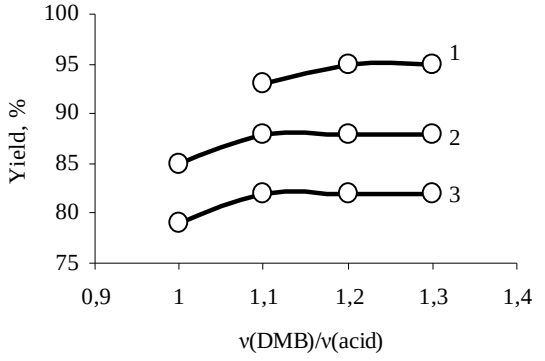


Fig. 4. Dependence of 3,4-DMACHA yield upon reagents ratio: AA (1); MAA (2) and EAA (3)

We studied the interaction of DMB with MAA and EAA at 388 K because they react slower at such temperature (Fig. 5). The increase of alkyl substituent at α-position of acrylic acid retards the reaction because of steric barriers. Therefore further we carried out the experiments within the temperature range of 413–433 K.

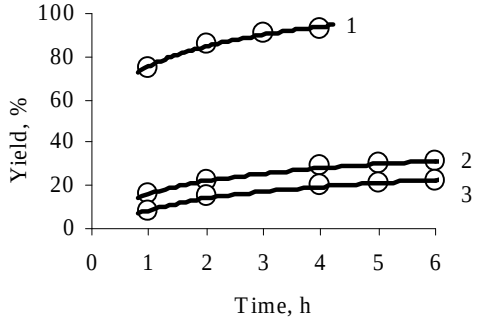


Fig. 5. Dependence of 3,4-DMACHA yield upon the length of alkyl radical of α-alkylacrylic acid: 3,4-DMCHA (1), 1,3,4-TMCHA (2) and 3,4-DM-1-ECHA (3). Temperature is 388 K, molar ratio DMB : acid = 1.2:1

The increase of reaction temperature increases the rate of DMB-MAA interaction and at 423 K the reaction comes to the end after 5–6 h. The same regularity is observed at DMB-EAA interaction. Moreover, the increase of alkyl radical decreases the yield of the main product – 88 % for 1,3,4-trimethylcyclohex-3-ene carbonic acid and 82 % for 3,4-dimethyl-1-ethylcyclohex-3-ene carbonic acid.

4. Conclusions

The effect of reagents ratio, temperature, amount of solvent and inhibitor on the yield of 3,4-dimethyl-1-alkylcyclohexenic acids was studied. At the interaction between DMB and AA without the solvent the yield of 3,4-dimethylcyclohex-3-ene carbonic acid is considerably less than that obtained in the presence of toluene. Studying the ratio toluene : reagents were established that maximum yields of the corresponding main products are achieved at the ratios (vol.) toluene : reagents = 2:1 and DMB : acid = 1.2:1.

At the interaction between DMB and acrylic acids within the range of 368–433 K the maximum yield of 3,4-dimethylcyclohex-3-ene carbonic acid (95 %) is achieved at 388 K and the maximum yield of 1,3,4-trimethylcyclohex-3-ene carbonic acid and 3,4-dimethyl-1-ethylcyclohex-3-ene carbonic acid (88 and 82 %, relatively) – at 423 K.

The structure and physico-chemical characteristics of the synthesized compounds were established.

References

[1] Lesnikova N., Byrdina N., Rogkova R. *et al.*: VIII Vsesouznaya Conf. po Khimii Org. Peroxidov. Leningrad 1985, 25.
[2] Dennis H., Olivir M. and Raed A.: Pat. USA 20100197960. C07C61/22, Publ. May 08, 2010.
[3] Petrov A. and Sonov N.: Zh. Obshchei Khimii, 1948, **18**, 1781.
[4] Liukas H. and Pressman D.: Ind. Eng., 1939, **10**, 142.
[5] Kreshkov A.: Osnovy Analiticheskoi Khimii. Khimiya, Moskwa 1976.
[6] Poliova I., Marshalok G., Fedevych M. *et al.*: Pat. Ukrainy MPK C07C11/00, Publ. Jan. 11, 2010.
[7] Denis G., Pikh Z., Yatchyshyn I. and Tolopko D.: Auth.Cert. SSSR. MKP C07C57/03, C07C57/055, Publ. Jan. 23, 1981.

α-НЕНАСИЧЕНІ КИСЛОТИ В РЕАКЦІЇ ДІЛЬСА-АЛЬДЕРА

Анотація. *Досліджено вплив природи і кількості розчинника та інгібітора, молярного співвідношення реагентів і температури на вихід алкілциклогексенових кислот при одержанні їх за реакцією Дільса-Альдера, виходячи з 2,3-диметилбута-1,3-дієну і алкілакрилових кислот. Встановлено будову та фізико-хімічні характеристики синтезованих речовин.*

Ключові слова: *2,3-диметилбута-1,3-дієн, α-акрилові кислоти, реакція Дільса-Альдера, 3,4-диметил-1-алкілциклогексенові кислоти.*