

THE SYNTHESIS OF 12-CYANODODECANOIC ACID FROM ERUCIC ACID

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The erucic acid isolated from acids mixture of rape seed oil was applied as a substrate to the synthesis of 12-cyanododecanoic acid. First the nitrile of erucic acid was got by passing ammonia through molten erucic acid, than its ozonolyses was performed.

INTRODUCTION

Erucic acid — the main component of rapeseed oil fatty acids — is the subject of our interest because there is a possibility of receiving from it compounds usable in chemical industry. Erucic acid nitrile is one of those derivatives which can be directly applied or be used as a intermediate substance in chemical synthesis.

Fatty acids nitriles are applied as plasticizers to synthetic plastics, rubber softeners, additives to lubricants and intermediate products to the synthesis of high molecular compounds as for example nylon.

A lot of publication like Ralston's and co-workers [6], Reuteneur's and Paquet's [7] concern that subject.

The latter have received, among others, erucic acid nitrile by passing ammonia at 280°C through molten erucic acid.

The yield depends on a lot of parameters as the reaction temperature, ammonia flow rate through molten fatty acids and type of catalyst used. The objective of the presentied work was a more distinct investigation of the above mention parameters and their influence on the synthesis of erucic acid nitrile. Secondly the erucic nitrile was oxidatively ozonolysis to obtain the 12-cyanodecanoic acid. As it is known, the ozonolysis of unsaturated fatty acids leads to receiving of, ω -functional compounds and their functions depend on the type of o-

zonolysed substance and depend on the way of ozonides decomposition.

Two research centres a French [3-5] one in Marseilles and an American [2] in Peoria studied the question of fatty acids ozonolysis and their derivatives. Oleic acid and its derivatives were the main subject of interest in those laboratories. Ozonolysis of erucic acid and its derivatives were studied too.

In our study the parameters published till now were used but some modifications were introduced to receive better results.

EXPERIMENTAL

Erucic acid nitrile was obtained by passing ammonia through molten 98% erucic acid isolated from the rapeseed oil fatty acids mixture by crystallization from solvents.

The apparatus to obtain the erucic acid nitrile consisted of round-bottomed flask fitted with an electric heater thermometer, ammonia inlet and a heating column packed with glass tubes to pass nonreacted ammonia through. 150 g of erucic acid was used to the reaction. The progress of the reaction was observed by means of TLC. After completing the process, the reaction mixture was multiple washed by water to get the neutral reaction and next dried by anhydrous sodium sulphate. Crude erucic acid nitrile was of pungent smell and dark brown colour.

The influence of ammonia flow rate, the process temperature and presence of dehydrating agent on the reaction time and yield was investigated. Each sample was weighted and analyzed by TLC method to determine the yield.

Table 1

The effect of ammonia flow rate and SiO₂ presence on reaction time and yield of erucic acid nitrile

Ammonia flow rate (l/h)	SiO ₂	Total reaction time (h)	Content of erucic acid nitrile in the reaction mixture (%)	Yield of erucic acid nitrile (%)
8	—	10.0	94.0	66.8
8	+	7.0	94.9	70.9
10	—	7.5	94.4	70.1
10	+	5.5	96.3	75.0
14	—	6.5	97.1	69.5
14	+	4.5	97.2	74.9

Reaction temperature — 280°C, erucic acid — 150 g, SiO₂ — 10 g.

The analysis of data compiled in Table 1 shows that the increase of ammonia flow rate through the reaction mixture appreciably shortens the reaction time. The similar action is observed when a dehydrating agent is introduced to the reaction flask. The shortening of the reaction time has a favourable effect on the quality of the obtained product and the yield of the process.

The process had the most favourable course at ammonia flow rates of 10 and 14 l/h. At these values the effect of temperature on the yield and the time of the process has been studied. On the analysis of the data compiled in the Table 2, a considerable shortening of the reaction time with the increase of temperature can be observed. The increase of temperature in the studied interval of 260-300°C does not appreciably effect erucic acid nitrile content in the reaction mixture.

This was due to two factors: temperature and reaction time. They have opposite effect on the final result of the process. The higher the temperature is, the greater is the probability of side-reactions. Simultaneously, the application of higher temperature shortens the reactions time what in turn has a favourable influence on the final result.

Table 2

The effect of reaction temperature on the yield of erucic acid nitrile

Ammonia flow rate (l/h)	Reaction temperature (°C)	Total reaction time (h)	Content of erucic acid nitrile in the reaction mixture (%)	Yield of erucic acid nitrile (%)
10	260	15.0	94.9	67.3
10	280	7.5	94.4	70.1
10	300	5.0	93.2	81.0
14	260	12.0	97.5	68.3
14	280	6.5	97.1	69.5
14	300	3.5	96.6	78.0

As it can be observed from the data in Table 2, the close contents of erucic acid nitrile in the product of the reaction have been obtained for the flow rate of 10 l/h irrespective of the temperature change.

The shortening of the reaction time elevates the reaction yield due to the decrease of the reaction mass dispersed by the ammonia stream. The crude nitrile of erucic acid was distilled under vacuum and a distillate was obtained of 100% purity when analyzed by TLC. Gas chromatography analysis showed presence of eicosanoic acid nitrile below

1%. Erucic acid nitrile obtained in above described way was oxidatively ozonized. GDR made apparatus LOZ-3 was applied as the ozone generator. Its characteristic: supplied voltage — 220 V, ozone yield-20-50 g/h, ozone concentration 5-10%. Chloroform, water and acetone containing 15-70% of H₂O were applied as the solvents of erucic acid nitrile during the ozonolysis. Ozonization temperature was changed in range from —10°C +35°C and the concentration of erucic acid nitrile in the solvent was 5-60%.

The ozonization was carried out at a threenecked flask. The ozone was supplied by the bubbler after reaching respective temperature of the reaction mixture. The end of the ozonization was proved by the bromic test. Then oxygen was passed through the mixture and the temperature was increased very slowly up to 95°C. That temperature was kept until complete decomposition of ozonides. The influence of various parameters on the ozonolysis yield is shown in Tables 3, 4, 5.

Table 3

The effect of ozonized solution concentration and temperature on the ozonolysis yield (solvent: chloroform)

Concentration of erucic acid nitrile in CHCl ₃ (g/100 ml)	Yield of 12-cyanododecanoic acid (%)		
	—10°C	0°C	+10°C
5	77.3	70.2	70.0
10	74.0	67.4	66.7
15	69.8	66.5	65.8
20	69.2	66.0	65.0

From the data inserted in Table 3 it comes out that lowering of ozonization temperature causes greater yields. The differences in yields are not great at applied temperature range —10°C to +10°C. More distinct influence is caused by changes of concentration of erucic acid nitrile in the reaction mixture. If acetone containing 15% H₂O was used as a solvent, the ozonolysis was carried at higher temperatures and higher concentration of erucic acid nitrile (Table 4). It may be seen that higher concentration of erucic acid nitrile caused the yield diminishing but even at 60% concentration and temperature of +35°C, the obtained yield was above 50%.

The results inserted in Table 5 prove that the increase of water concentration in the solvent does not cause a distinct lowering of the yield. It means that erucic acid nitrile ozonization — analogously as

Table 4

The effect of ozonized solution concentration and temperature on the ozonolysis yield (solvent: acetone containing 15% H₂O)

Concentration of erucic acid nitrile (%)	Yield of 12-cyanododecanoic acid (%)		
	10°C	25°C	35°C
20	71.7	65.6	62.9
40	66.6	63.2	63.0
60	65.6	59.7	55.4

Table 5

The influence of water in acetone on the yield of 12-cyanododecanoic acid

Solvent	Yield of 12-cyanododecanoic acid (%)
Acetone with 15% H ₂ O	63.2
Acetone with 30% H ₂ O	56.3
Acetone with 50% H ₂ O	55.9
Acetone with 70% H ₂ O	62.2
Water	58.6

Concentration of erucic acid nitrile — 40%, ozonization temperature — 25°C.

that of erucic acid or its ester can be carried out in aqueous medium. But water causes increasing of reaction mass viscosity and that in turn makes difficult the contact ozone/erucic acid nitrile and so the reaction time gets longer.

Isolation of 12-cyanododecanoic acid from the reaction mixture and extraction of the nonacidic substances and then acidification of salts and extraction of ω -cyanocarboxylic compounds were not successful in case of erucic acid nitrile though good results were observed for oleic acid nitrile. Therefore the following procedure was applied: the reaction mixture was left for 12 hours at 0°C, filtered and washed with water.

The crude 12-cyanodecanoic acid contained 75.0–80.0% of pure substance and the yield was 50%. Double crystallization from cyclohexane enabled receiving a 96.6% pure 12-cyanododecanoic acid with 85% yield. The analysis by GLC proved the presence of two substances characterized by shorter retention time than 12-cyanododecanoic acid.

Above presented way was applied for receiving from erucic acid such a compound which contains a cyano group and carboxylic group. That compound is an intermediate product to the synthesis of high molecular compounds e.g. nylon 13 and 1313. The optimum parameters of that compounds synthesis were established too.

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OTRZYMANIE KWASU 12-CYJANOUNDEKANOKARBOKSYLOWEGO Z KWASU ERUKOWEGO

Streszczenie

Kwas erukowy wyodrębniony z mieszaniny kwasów oleju rzepakowego zastosowano jako substrat do syntezy kwasu 12-cyjanoundekankarboksyłowego.

W tym celu otrzymano nitril kwasu erukowego, przepuszczając amoniak przez stopiony kwas erukowy. Zbadano wpływ temperatury reakcji na czas i wydajność procesu (260°C, 280°C i 300°C). Postęp reakcji śledzono przy pomocy TLC. Otrzymany nitril kwasu erukowego poddano ozonolizie. Zbadano wpływ temperatury, rozpuszczalnika i koncentracji mieszaniny reakcyjnej na wydajność reakcji. Wyodrębnienie czystego kwasu 12-cyjanoundekankarboksyłowego przeprowadzono na drodze jego krystalizacji wprost z mieszaniny reakcyjnej, a następnie rekrytalizacji z rozpuszczalnika.

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ПОЛУЧЕНИЕ 12-ЦИАНОУНДЕКАНОКАРБОНОВОЙ КИСЛОТЫ ИЗ ЭРУКОВОЙ КИСЛОТЫ

Резюме

Эруковую кислоту выделенную из смеси кислот рапсового масла применяли как субстрат для синтеза 12-цианоундеканокановой кислоты.

С этой целью получали нитрил эруковой кислоты, пропуская аммиак через расплавленную эруковую кислоту. Исследовали влияние температуры реакции на продолжительность и производительность процесса (260°C, 280°C и 300°C). Ход реакции наблюдался с помощью ТСЛ. Полученный нитрил эруковой кислоты подвергали анализу. Исследовали влияние температуры, растворителя и концентрации реакционной смеси на производительность реакции. Выделение чистой 12-цианоундеканокановой кислоты происходило путем ее кристаллизации непосредственно из реакционной смеси, с последующей рекристаллизацией из растворителя.