EUROPEAN QUALIFYING EXAMINATION 2003

PAPER A
CHEMISTRY

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LETTER FROM THE APPLICANT

As you are aware, we have substantial interests, through a joint venture, in the preparation of reusable plastic bottles. A published set of experiments has shown that the most suitable plastic for making reusable bottles is polyethylenenaphthalate (PEN). A bottle that is going to be reused has to be cleaned and sterilised at high temperatures. Bottles made from PEN are much better able to withstand these high temperatures than bottles made from other known plastics.

We have not yet been able to commercialise PEN bottles, because up to now the cost of making PEN has always been too high. The high cost of PEN follows directly from the difficulty in making the key precursor: 2,6-dimethylnaphthalene (2,6-DMN). A number of synthetic routes to 2,6-DMN have been published. The known routes all have at least one of the following problems:

a) The route uses expensive precursors.

b) The route is a multistage reaction, consisting of four or five reaction steps.

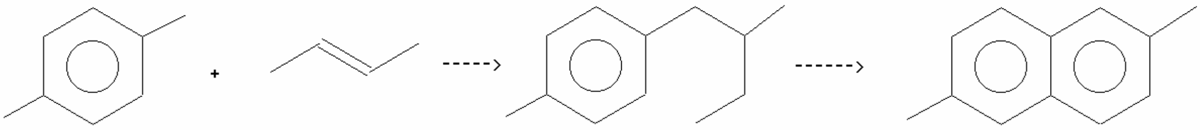
c) The reactions used are not selective and produce a lot of side products, which are typically very difficult to separate from 2,6-DMN.

We have succeeded in finding a way to manufacture 2,6-DMN by an economic and simple process which starts from a cheap precursor and is selective and involves a minimum number of steps. On the following pages we have described our process in more detail. Please file a European patent application based on this information. If need be, more than one application may be filed. Copies of what we think is the closest state of the art are also provided.

The process we have developed comprises the following steps:

- the reaction between para-xylene (p-xylene) (I) and butene (II) to produce p-(2-methylbutyl)-toluene (III)
- dehydrocyclisation of p-(2-methylbutyl)-toluene to produce 2,6-dimethylnaphthalene (2,6-DMN (IV)).

A simplified illustration of the reaction scheme is presented below:



(I) (II) (III) (IV)

Each of the steps will now be described:

I. Preparation of p-(2-methylbutyl)-toluene (III)

In the first step an alkylation reaction is performed in which p-xylene is reacted with butene. The alkylation reaction adds a butyl group to a methyl group on the xylene. This reaction can form products with either a straight side chain (in which case the reaction product is p-(n-pentyl)-toluene) or a branched side chain (in which case the product is the desired p-(2-methylbutyl)-toluene). Depending on the precise catalyst used, the ratio between the branched and straight-chained products varies somewhat. It is very important in our reaction scheme to avoid as far as possible the formation of straight chained products such as p-(n-pentyl)-toluene. If significant amounts of p-(n-pentyl)-toluene are formed, this compound has to be removed (e.g. by fractional crystallisation) before the dehydrocyclisation step. If p-(n-pentyl)-toluene is present during the dehydrocyclisation reaction significant amounts of isomers of 2,6-DMN will be produced. It is very difficult to separate 2,6-DMN from these isomers.

In order to minimise the formation of straight-chained products the reaction has to be performed in the presence of a supported alkali metal catalyst. In principle all alkali metals can be used, it is however preferred for economic reasons to use sodium, potassium or a mixture of these two metals. The metals have to be used on a support. The reaction may be performed with the alkali metal supported on standard supports. The highest yields of p-(2-methylbutyl)-toluene (III) are obtained when the support itself is basic.

We define a basic support to be a material, which desorbs carbon dioxide at a temperature higher than a standard alpha-alumina. The procedure for measuring this desorption temperature and the precise nature of the standard alpha-alumina to be used are set out in the patent US-A-1 000 000.

Particularly preferred basic supports are powdered sodium or potassium carbonate since when catalysts having these supports are used, virtually no p-(n-pentyl)-toluene will be formed. In this case no separation step is necessary.

A. Preparation of the catalyst

A supported alkali metal catalyst suitable for our reaction can be prepared by introducing the alkali metal and the support in a weight proportion of 1 part metal to 0.5 - 500 parts of support into a closed vessel containing an organic solvent under an inert atmosphere. The resulting mixture is stirred at high speed at a temperature typically between 30 and 60°C for 1 to 5 hours. The organic solvent used is preferably one of the reactants.

Example

3 parts of metallic sodium and 97 parts of potassium carbonate were simultaneously charged into 200 parts of p-xylene. The mixture is heated to 50°C and stirred at high speed for 2 hours.

B. Preparation of p-(2-methylbutyl)-toluene

The reactants should be dry. If necessary, a drying step is to be included. The reaction system should be free of oxygen. The reaction is usually performed at a temperature between 100 and 200°C. Below 100°C, the reaction is too slow. Above 200°C, the selectivity decreases. The preferred temperature range is from 110 to 180°C. A reaction time of from 1 to 10 hours has typically been used. The process can be operated continuously in a tubular reactor or discontinuously in a batch reactor. When the catalyst becomes less active, it can be taken out of the system and replaced.

…/…

Example

The sodium supported on potassium carbonate catalyst obtained in the example above (suspended in p-xylene) is introduced into a reactor kept at 120°C. Additional p-xylene is added to obtain a weight proportion p-xylene to catalyst of 10:1. Butene is then slowly bubbled through the reactor for 5 hours. The p-(2-methylbutyl)-toluene product is filtered from the catalyst. The product can be passed directly to the dehydrocyclisation step without further purification.

II. Dehydrocyclisation to 2,6-dimethylnaphthalene (IV)

This reaction is performed in the gas phase, using a solid catalyst. Many commercially available catalysts can be used. The most suitable catalysts are based on metals of the platinum group (for example platinum or palladium) supported on an oxide such as chromium oxide, alumina, silica or a zeolite. The reaction is well known in the literature, and it is not necessary to describe it in more detail. We have used catalysts comprising platinum supported on a zeolite in our experiments since these catalysts were available in our plant.

A. Preparation of the catalyst

A platinum on zeolite Y catalyst can be used. This catalyst may be prepared by any of the known processes. Typically the catalyst is prepared by impregnating the zeolite with a solution of a platinum compound until a paste is formed, extruding the paste as pellets, drying the pellets (a few hours at a temperature slightly above 100°C) and calcining the dried pellets (at least 3 hours in air at 500 to 600°C). The platinum content should be in the range 0.5 to 2.5% by weight of the catalyst.

B. Preparation of 2,6-DMN

The dehydrocyclisation process may be performed by passing a gas containing hydrogen and p-(2-methylbutyl)-toluene (III) at a temperature in the range of 150 to 400°C, preferably between 200 and 300°C over the catalyst. In order to avoid side reactions, an inert gas, such as nitrogen, carbon dioxide or steam is often added.
In order to make it simpler to uniformly transfer the solid starting material into the gas phase, it can be dissolved in a solvent such as an aromatic (benzene, toluene) or aliphatic hydrocarbon (hexane, heptane). 2,6-DMN can be condensed from the gas.

Example

A platinum on zeolite catalyst was put into a 3 mm quartz tube. Then p-(2-methylbutyl)-toluene (III) and a 1:1 nitrogen:hydrogen mixture were introduced. The reaction conditions are: temperature 310°C, pressure 1 bar, contact time 0.8 sec. The yield of 2,6-DMN was 77.5%.

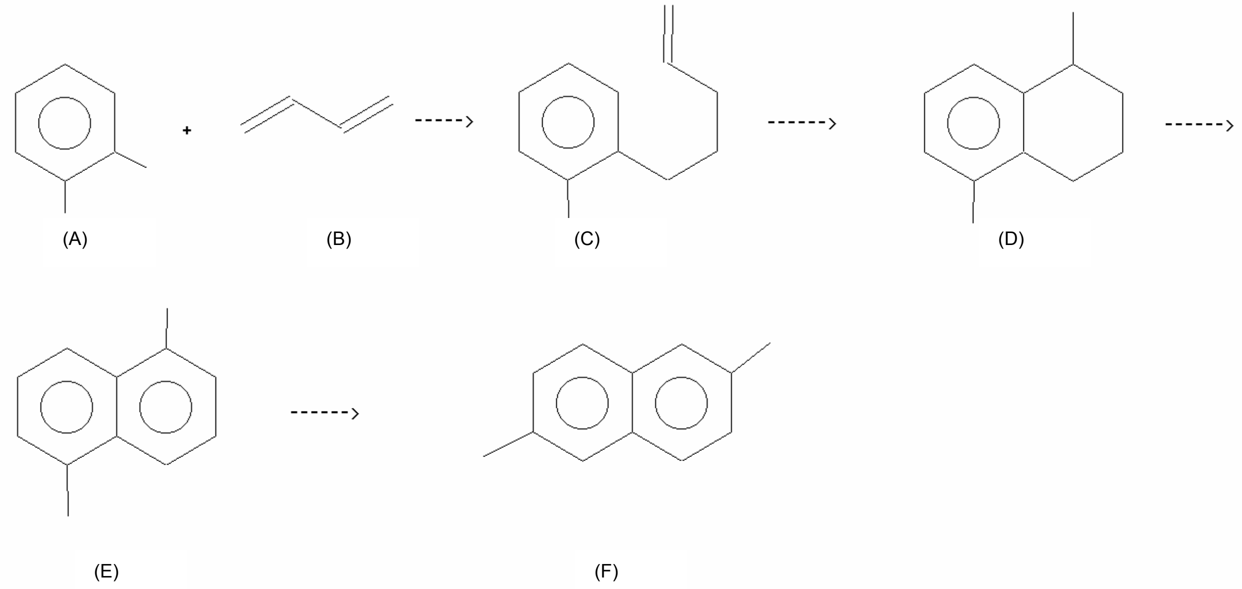
III. **Purification of the product**

The product obtained from the dehydrocyclisation contains some impurities, and can be purified by distillation.

DOCUMENT 1 (State of the art)

The present application relates to a process for making dialkylnaphthalenes from alkylbenzenes. Alkylbenzene starting materials include: toluene, ethylbenzene and ortho-, para- and meta-xylene (o-, p- or m-xylene). In the first stage of the reaction the alkylbenzenes are reacted with alkenes such as butene or conjugated dienes such as 1,3-butadiene or isoprene, in the presence of sodium metal supported on an acidic support, such as acidic silicas. An acidic support is a material, which desorbs carbon dioxide at a temperature lower than a standard alpha-alumina. The procedure for measuring this desorption temperature and the precise nature of the standard alpha-alumina to be used are set out in the patent US-A-1 000 000.

The product is a modified alkylbenzene if an alkene is used, or an alkenylbenzene if a conjugated diene is used. Examples of this reaction include the reaction of butene or 1,3-butadiene with p-xylene or the reaction of 1,3-butadiene with o-xylene.
The alkylbenzenes or alkenylbenzenes are cyclised in a second stage to give dialkyltetralines. The dialkyltetralines can be dehydrogenated to produce dialkyl-naphthalenes. The resulting dialkylnaphthalenes can be isomerised to produce other isomers. If o-xylene (A) and 1,3-butadiene (B) are used as the starting materials then this reaction scheme provides an economically viable route for producing 2,6-dimethyl-naphthalene. This particular scheme is illustrated and exemplified below:



Example

Catalyst preparation

Dry high purity nitrogen was blown into o-xylene (boiling point: 144°C). Sodium metal was added under rapid stirring. This suspension was mixed with acidic, anhydrous silica with rapid stirring at 50°C. The solvent was distilled off at 145-170°C, leaving behind a catalyst consisting of sodium metal supported on the silica.

Reaction

The catalyst (5 g) was stirred into o-xylene (1 mol) and heated to 140-145°C over a period of 1 hour. 1,3-butadiene (0,1 mol) was introduced over a period of 3 hours. The reaction mixture was subsequently cooled to 100°C and left to stand for 30 min. The liquid phase was filtered from the catalyst and the product was separated by distillation at a pressure of 3 kPa. The liquid product contained 88,1% of 5-(o-tolyl)-pentene (C). The main side product was o-(2-methylbutenyl)-toluene. Cyclisation of (C) in toluene solution by heating with a solid phosphoric acid catalyst and dehydrogenation of the resulting 1,5-dimethyltetralin (D) over a catalyst consisting of 0.3% of platinum supported on alumina under hydrogen at 400°C gave 1,5-dimethylnaphthalene (E).

The 1,5-dimethylnaphthalene was isomerised in the presence of an alumina-bonded mordenite catalyst at 350 - 400°C to give a mixture containing 10% 1,5-dimethylnaphthalene, 43% 2,6-dimethylnaphthalene (F), 44% 1,6-dimethylnaphthalene and 3% other compounds. The 2,6-dimethylnaphthalene can be separated by chromatography.

Claims

1. A process for making dialkylnaphthalenes comprising the following steps:

   (a) Reaction of an alkylbenzene with an alkene or a conjugated diene in the presence of a catalyst consisting of sodium metal supported on an acidic support,

   (b) cyclisation of the product thus obtained to produce a dialkyltetraline, and

   (c) dehydrogenation of the dialkyltetraline to dialkylnaphthalene.

2. A process in accordance with claim 1 in which the dialkylnaphthalene product is isomerised.

DOCUMENT 2 (State of the art)

We have developed a process for efficiently producing 2,6-dimethylnaphthalene which comprises subjecting p-(2-methylbutyl)-toluene or p-(2-methylbutenyl)-toluene as the starting material to a dehydrocyclisation reaction in the presence of a catalyst comprising a supported platinum group metal. The metal is typically platinum or palladium at 0.5 to 2.5% by weight of the catalyst. Any support may be used including alumina, silica, a zeolite (such as zeolite Y), or chromium oxide. The above process enables the production of highly pure 2,6-dimethylnaphthalene in a high yield and at a low cost.

The dehydrocyclisation process is performed by passing a gas containing hydrogen and the starting material over the catalyst at a temperature in the range of 150 to 400°C, preferably between 200 and 300°C. In order to avoid side reactions, an inert gas, such as nitrogen, carbon dioxide or steam is added. The resulting 2,6-DMN is condensed from the gas. In order to make it simpler to uniformly transfer the solid starting material into the gas phase, it can be dissolved in a solvent such as an aromatic (benzene, toluene) or aliphatic hydrocarbon (hexane, heptane).

FAX FROM THE APPLICANT

URGENT !!!

Re: Our patent application sent to you last Friday
(process for preparing 2,6-DMN)

Shortly after sending you the request for drafting the said application, the project leader informed me that additional tests have been done concerning the first (alkylation) step of our process. It appears that the reaction used in this step can be used in other economically very interesting processes.

We have determined that the alkylation reaction can be performed with any alkylbenzene and any alkene in the presence of a supported alkali metal catalyst to produce alkylated products. In addition a conjugated diene (such as 1,3-butadiene) can be reacted with an alkylbenzene using the same catalyst in which case the reaction product is an alkenylbenzene.

The tests indicate that, irrespective of whether the starting product is an alkene or a conjugated diene, the precise choice of the catalyst support influences the ratio of branched to straight-chained products in precisely the same manner as we have observed for the reaction between p-xylene and butene.

Alkenylbenzenes can be dehydrocyclised to produce substituted naphthalenes using precisely the same catalysts and reaction conditions as alkylbenzenes.

These tests have led us to the important realisation that 1,3-butadiene can be used as a starting material instead of butene in our process for making 2,6-DMN. In this case the product of the first step in our process will be p-(2-methylbutenyl)-toluene). This compound can be dehydrocyclised to 2,6-DMN under precisely the same conditions as p-(2-methylbutyl)-toluene). The use of 1,3-butadiene is commercially very interesting and should be protected if possible.

I hope this information can be taken into consideration when drafting the application.