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NITRATION OF ALKYL BENZENES WITH NITRIC AND PHOSPHORIC ACIDS

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ABSTRACT OF THE DISCLOSURE

This disclosure teaches a process for nitrating alkyl-substituted aromatic compounds (particularly toluene) in such a manner that a greater yield of p-isomers is obtained, as compared with o and m-isomers, than had heretofore been achieved. Nitration is here carried out with nitric acid in the presence of phosphoric acid. The concentration and quantity of the phosphoric acid are chosen in such a way that after the reaction the P_2O_5 content thereof is not more than 82% and preferably between 62% and 76%. Sulphuric acid may also be present, preferably with its quantity not more than 80% that of phosphoric acid.

BACKGROUND OF THE INVENTION

Usually nitrations of aromatic compounds have been carried out with the use of a mixture of nitric acid and sulphuric acid, and in the mononitro compounds formed, the portion of o-isomers has generally been largest. Thus, for instance, when nitrating toluene, the ratio by percentage among o, m and p-nitrotoluene has been approximately 58.5/4.5/37.0. This isomer relationship has been almost independent of the reaction conditions.

During recent years, however, there has been an increased demand for p-nitrotoluene, for instance as a raw material for optical brighteners. There has also been an increased demand for the p-isomer for other mononitro alkyl benzenes. Thus, p-nitroethyl-benzene for example has become an important raw material for chloro-amphenicol, an antibiotic. Accordingly, it has become of interest to endeavor to carry out nitration of aromatic compounds in such a way that an increased yield of p-isomer is obtained. Among other things, it has been proposed to use a sulphonated ion exchanger or aromatic sulphonic acids instead of sulphuric acid. These methods have also led to a greater yield of p-isomer, but they have proven to be uncertain when used on an industrial scale, among other things owing to the difficulty in recovering and recirculating the comparatively expensive auxiliary chemicals. Another proposal for achieving a higher yield of p-isomer involves nitration with alkyl nitrates in the presence of polyphosphoric acid. This method cannot have any commercial significance either, because it is altogether too expensive. Attempts have also been made to nitrate toluene with nitric acid in the presence of polyphosphoric acid, whereby a certain although somewhat smaller increase of p-nitrotoluene yield has been obtained. In these attempts it has proven to be most appropriate to use polyphosphoric acid with a concentration corresponding to 83% phosphorus pentoxide (P_2O_5). The explanation of the effect of the polyphosphoric acid on the isomer ratio must in all probability be that the primary attack at the nitration was obtained through a nitronium ion, which exists in association with a molecule of a polymer phosphoric acid. The great space which such an association product requires has been assumed to involve a steric hindrance for the nitration in o-position to the alkyl group. The use of polyphosphoric acid in accordance with

what is mentioned above does not lead to any industrially useful methods, among other things owing to the undesirable dinitration that takes place. This dinitration is associated with, among other things, difficulties in obtaining efficient stirring. Furthermore, it has proven to be difficult to recover spent acid, among other reasons, owing to difficult corrosion conditions, and as a consequence of this very complicated and expensive apparatus would have to be employed.

SUMMARY OF INVENTION

Through the present invention, it has become possible to carry out nitration of alkyl-substituted aromatic compounds in a way that can be performed technically, so that a greater yield of p-isomer is obtained than when earlier methods are used. Through the method, according to the present invention, it is possible in a simple and economically satisfactory way to carry out nitrations of the desired kind, without any inconveniencing quantities of undesirable dinitro compounds arising, and without encountering any particular difficulties in the recovery of the spent acid. It has been discovered, quite unexpectedly, that the desired increase of the yield of p-nitro alkyl benzene can be obtained with phosphoric acid of a considerably lower concentration than has previously been known, and the desired effect can be obtained at P_2O_5 contents corresponding to pure ortho-phosphoric acid, or, in fact, diluted ortho-phosphoric acid of ordinary commercial quality. At the same time, it has been discovered, quite unexpectedly, that the desired increase of the yield of p-isomer is retained if the nitration is carried out in a mixture of phosphoric acid and sulphuric acid.

DESCRIPTION OF THE PREFERRED EMBODIMENT

When nitrating in the presence of phosphoric acid, as well as in the presence of sulphuric acid, it is the composition of the spent acid obtained that is decisive for the result of the nitration. In the following, the P_2O_5 content of the phosphoric acid which is present in the spent acid (i.e. the part of the spent acid which does not consist of nitric acid) has been designated as the "P_2O_5 content in the spent acid," which corresponds to the mode of expression that is the practice in conventional nitration in the presence of sulphuric acid.

The method of nitrating alkyl-substituted aromatic compounds, particularly toluene, in such a way that a greater portion of p-isomer is obtained than when earlier methods are used, is characterized according to the present invention in that the nitration is carried out with nitric acid in the presence of phosphoric acid, the concentration and quantity of which is chosen in such a way that after the reaction the P_2O_5 content of the phosphoric acid to not more than 82%. The phosphoric acid should particularly be chosen so that the P_2O_5 content after the reaction does not exceed 76%, and it can appropriately amount to between 62 and 76%. It can also be appropriate that the acid mixture used for the nitration also contains sulphuric acid, and the quantity of sulphuric acid should then amount to not more than 80% of the quantity of phosphoric acid.

The invention will now be described in more detail, with reference to some experiments, accounted for as examples of carrying out the method.

Examples 1–7

In Example 1, to 5.65 g. of toluene there was added during the course of 15 minutes and with intensive stirring, 41.5 g. of nitration acid, consisting of 4 g. of 99% nitric acid and 37.5 g. of phosphoric acid containing 73% P_2O_5. The stirring was thereafter continued for 40

minutes, and during the whole of the experiment the temperature was kept at 30±1° C. The reaction mixture was thereafter poured out on 400 g. of ice, after which extraction with 3× 20 ml. of chloroform took place. The chloroform phase was thereafter washed with water and analyzed with gas chromatography.

The results of the experiment will be noted from the attached table, in which 6 other experiments have likewise been accounted for, which other experiments were carried out in an entirely similar way, but in which there were certain variations as regards the molar ratio between nitric acid and toluene and the concentration of phosphoric acid and the reaction temperature. Thus, in Example 1, a molar excess of approximately 2% of nitric acid in relation to the toluene was used, while for experiments 2–7, nitric acid with approximately 6% deficit was used.

As will be noted from the table, at Example 1, a considerably greater portion of p-isomer was obtained than at the conventional nitration with nitric acid and sulphur acid, in which the ratio p-nitrotoluene (PNT) to o-nitrotoluene (ONT) is approximately 0.63, while said ratio in Example 1 amounted to 1.11.

In Example 2, the P_2O_5 content of spent acid is 62.7, and even at this low concentration, there is a noticeable improvement as regards the increased yield of p-isomer.

In Example 3, the P_2O_5 content in the spent acid has been increased to 69.0%, and thereby also a considerable improvement of the yield of p-isomer has been obtained in relation to Example 2.

Also in Example 4, the increase of the P_2O_5 content in the spent acid (to 76.6) has increased the portion of p-isomer in the end product, but at the same time a certain, although comparatively small, quantity of dinitrotoluene (DNT) has been formed.

If, as in Example 5, the P_2O_5 content in the spent acid is allowed to amount to 82.0%, the quantity of dinitrotoluene will increase quite considerably, and therefore the P_2O_5 content must not be allowed to exceed 82%. In Example 5, the quantity of p-nitrotoluene in relation to the quantity of o-nitrotoluene has further increased, but this is associated with the fact that at the dinitration, which is not desired, it is particularly the o-nitrotoluene which is consumed.

Example 6 shows an experiment in which the reaction temperature has been reduced to 10° C., which does not seem to have had any noticeable effect on the relaiton between the quantities of p- and o-isomers.

In Example 7, finally, the reaction temperature has been increased to 70° C., and a comparison with Example 3 shows that the decrease in the relation of p-isomer to o-isomer is comparatively insignificant.

From the table, it can be seen that the P_2O_5 content in the spent acid should amount to not more than 82%, but should appropriately not be more than 76%, in order that the desired increase of the quantity of p-nitrotoluene may be obtained without altogether too great dinitration. It will also be noted from the table that the influence of the reaction temperature is insignificant when this is varied within reasonable limits. Nor does a slight excess or deficit of nitric acid seem to have any noticeable influence on the result.

Example 8

To 7.1 g. of ethylbenzene was added during the course of 15 minutes, with intensive stirring, 53 g. of nitration acid consisting of 4 g. of nitric acid and 49 g. of phosphoric acid with 76.7% P_2O_5. This involves that the molar ratio between the nitric acid and the ethylbenzene shows as deficit of nitric acid of approximately 5%. After the addition of the ingredients, the stirring was continued for 40 minutes, and during this time, as well as during the entire experiment, the temperature was kept at 30° C. In the same way as described in Example 1, the reaction mixture was thereafter poured out on ice and extracted with chloroform, after which the chloroform phase was washed with water and analyzed with gas chromatography. This analysis gave the following results:

	Percent
o-Nitro-ethylbenzene	40.6
m-Nitro-ethylbenzene	3.7
p-Nitro-ethylbenzene	55.7

The ratio of p/o-isomer thus became 1.37, which is considerably better than the result obtained at the nitration in the conventional way with nitric acid and sulphuric acid, at which said ratio will be approximately 1.08.

The P_2O_5 content in the spent acid amounted to 75.0%.

Example 9

To 7.1 g. of isopropylbenzene was added during the course of 45 minutes and with intensive stirring 53 g. of nitration acid with the same composition as per example 8, after which the stirring was continued for 10 minutes at 35–40° C. During the actual addition of the ingredients, the temperature was approximately 50° C. In this case, the gas chromatography gave a ratio between p/o-isomer of 3.03, which is considerably higher than the same value 2.08 for the corresponding conventional nitration with nitric acid and sulphuric acid.

For this experiment, a 10% excess of the nitric acid was used, and the P_2O_5 content in the spent acid was 76.3%.

Example 10

To 0.2 g. of toluene was added during the course of 15 minutes with intensive stirring 53 g. of nitration acid consisting of 4 g. of nitric acid and 49 g. of phosphoric acid with 82% P_2O_5. This addition of ingredients involves that to each mole of toluene is added approximately 29 moles of nitric acid. After the addition of the ingredients, the stirring was continued for 1 hour, and during the whole experiment the temperature was kept at 30° C. The P_2O_5 content in the spent acid was 81.45%. Through gas chromatography, the following composition of the product was obtained:

	Percent
2,6-dinitrotoluene (2,6-DNT)	9.6
2,4-dinitrotoluene (2,4-DNT)	86.4
Other dinitrotoluenes	4.0

Through the great excess of nitric acid, a dinitration of the toluene took place in this experiment, and the yield of 2,4-DNT was then considerably improved in relation to the corresponding conventional nitration with nitric acid and sulphuric acid, where approximately the following composition is usually obtained:

	Percent
2,6-DNT	20
2,4-DNT	76
Other dinitrotoluenes	4.0

Example 11

To 5 g. of o-nitrotoluene was added during the course of 15 minutes and with intensive stirring 53.6 g. of nitration acid consisting of 4.6 g. of nitric acid and 49 g. of phosphoric acid with 82.2% P_2O_5. This addition of ingredients involves that to each mole of o-nitrotoluene is added 2 moles of nitric acid. After the addition of the ingredients, the stirring was continued for 1 hour, and during the whole of the experiment the temperature was kept at 30° C. This P_2O_5 content in the spent acid was 81%. The analysis with gas chromatography gave the following results:

	Percent
2,4-DNT	72.9
2,6-DNT	27.1

At conventional nitration with nitric acid and sulphuric acid, the following is obtained:

	Percent
2,4-DNT	67
2,6-DNT	33

The portion of 2,4-DNT has thus, in the experiment here described, been improved in relation to the yield with conventional nitration.

Example 12

To 5 g. of raw m-nitrotoluene, consisting of

	Percent
MNT	93
ONT	2
PNT	5

was added during the course of 15 minutes and with intensive stirring, 53.6 g. of nitration acid with the same composition as per Example 11. This involves that for each mole of m-nitrotoluene was added 2 moles of nitric acid. The stirring after the addition of the ingredients was continued for 1 hour and the temperature during the whole of the experiment was kept at 50° C. The gas chromatography analysis gave the following composition:

	Percent
3,4-DNT	64.0
2,3-DNT	24.3
2,5-DNT	11.7

With the corresponding nitration carried out which conventional nitration acid consisting of nitric acid and sulphuric acid, the following result was obtained:

	Percent
3,4-DNT	49.9
2,3-DNT	38.0
2,5-DNT	12.0

If the compositions of the two products are compared, it will be clearly noted that the content of 3,4-DNT increased at the expense of the 2,3-DNT. The content of P_2O_5 in the spent acid was 81.0%.

Example 13

To 12 g. of toluene was added during the course of 15 minutes and with intensive stirring 57.9 g. of nitration acid consisting of 4 g. of nitric acid, 49 g. of phosphoric acid with 78.4% P_2O_5 and 4.9 g. of sulphuric acid (96.5%). This addition of ingredients involves that approximately 0.5 mole of nitric acid corresponded to each mole of toluene. After the addition of the ingredients, the stirring was continued for 40 minutes. During the whole of the experiment that temperature was kept at 30° C. Through gas chromatography the composition of the products was fixed at:

	Percent
ONT	40.4
MNT	4.3
PNT	51.6
DNT	3.7

Example 14

To 6.15 g. of toluene was added during the course of 15 minutes and with intensive stirring, 92.2 g. of nitration acid consisting of 4 g. of nitric acid, 49 g. of phosphoric acid with 75.2% P_2O_5 and 39.2 g. of sulphuric acid (96.5%). With this composition, there was thus an approximate 6% deficit of nitric acid in relation to the toluene. This stirring was continued for 40 minutes and the temperature was 30° C., and the P_2O_5 content in the spent acid was 71.4%. Gas chromatography showed the following product composition

	Percent
ONT	41.0
MNT	3.0
PNT	45.1
DNT	10.9

The ratio PNT to ONT was thus 1.10, or practically the same as for experiment 6, in which the P_2O_5 content of the spent acid was approximately the same. However, a comparatively significant formation of dinitrotoluene had taken place, and the addition of sulphuric acid corresponding to 80% of the phosphoric acid should therefore appropriately not be carried much farther.

An addition of sulphuric acid as described in the two last-mentioned experiments can be advantageous, as it prevents crystallization of the phosphoric acid, which can otherwise involve technical problems, particularly with P_2O_5 contents of between 78 and 82%.

From the experiments described above, it will be noted that even if the present method has its greatest significance for toluene, it can also be used to advantage for other alkyl-substituted aromatic compounds, for instance ethylbenzene and isopropylbenzene, and an increased yield of the p-isomer in relation to the result with conventional nitration with nitric acid and sulphuric acid is then obtained.

If the reaction is carried out so that dinitration takes place, an increased yield of 2,4-DNT will be obtained, and if the o-nitrotoluene and the m-nitrotoluene is nitrated according to the invention, the quantities of 2,4 and 3,4-DNT will increase. In all cases, the nitration in p-position will take place to a greater extent that at conventional nitration.

Nitration according to the invention can take place advantageously with a continuous procedure, and it has proven possible, for instance, for continuous mononitration of the toluene, to use apparatus which has originally been designed for conventional nitration with nitric acid and sulphuric acid.

Recovery of the phosphoric acid in the spent acid can, in principle, take place in the same way as for sulphuric acid, i.e. by heating and distilling off the water.

Ex.	Grams added			Reaction temperature, ° C.	Percent P_2O_5		Product composition, percent				Turnover of toluene percent	Ratio, PNT/ ONT
	Phosphoric acid	Nitric acid	Toluene		In phosphoric acid added	In spent acid	MNT	ONT	PNT	DNT		
1	37.5	4.0	5.65	30	73.0	70.8	4.3	45.1	50.2	0.0	99.6	1.11
2	66.0	4.0	6.15	30	63.5	62.7	4.5	55.6	39.9	0.0	56.0	0.72
3	49.0	4.0	6.15	30	70.4	69.0	5.6	47.9	46.3	0.0	86.7	0.97
4	49.0	4.0	6.15	30	78.4	76.6	4.0	42.5	52.2	1.3	96.0	1.23
5	49.0	4.0	6.15	30	83.9	82.0	3.7	31.5	47.8	17.0	95.0	1.52
6	49.0	4.0	6.15	10	73.0	71.5	4.2	44.8	50.6	0.4	90.0	1.13
7	49.0	4.0	6.15	70	72.0	70.4	5.8	48.1	46.1	0.0	95.0	0.96

The ratio of PNT to ONT is 1.28 or somewhat higher than as per Example 4, in which the P_2O_5 content of the spent acid was practically the same as for this experiment, in which it amounted to 76.4%. Thus, the addition of sulphuric acid corresponding to 10% of the phosphoric acid has not had any detrimental effect on the distribution of isomers, although there has been a certain, slight increase of the quantity of DNT.

It will be apparent to those skilled in the nitrating of alkyl-substituted aromatic compounds that deviations may be made from the disclosed examples without departing from the main theme of invention set forth in the following claims.

What is claimed is:

1. A process for nitrating an alkyl-substituted aromatic compound in such a way that the p-isomer yield

is optimized and comprising the step of carrying out the nitration with nitric acid in the presence of phosphoric acid, with the concentration and quantity of the phosphoric acid chosen in such a way that after the reaction the P_2O_5 content thereof is not more than 82%.

2. The process according to claim 1 with the P_2O_5 content not more than 76%.

3. The process according to claim 2 with the P_2O_5 content between 62% and 76%.

4. The process according to claim 1 with the alkyl-substituted aromatic compound toluene.

5. The process according to claim 2 with the alkyl-substituted aromatic compound toluene.

6. The process according to claim 3 with the alkyl-substituted aromatic compound toluene.

7. A process for nitrating an alkyl-substituted aromatic compound in such a way that the p-isomer yield is optimized and comprising the step of carrying out the nitration with nitric acid in the presence of phosphoric acid and sulphuric acid, with the concentration and quantity of the phosphoric acid chosen in such a way that after the reaction the P_2O_5 content thereof is not more than 82%.

8. The process according to claim 7 with the P_2O_5 content not more than 76%.

9. The process according to claim 7 with the P_2O_5 content between 62% and 76%.

10. The process according to claim 7 with the quantity of sulphuric acid not more than 80% that of phosphoric acid.

11. The process according to claim 8 with the quantity of sulphuric acid not more than 80% that of the phosphoric acid.

12. The process according to claim 9 with the quantity of sulphuric acid not more than 80% that of the phosphoric acid.

References Cited

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