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MONONITRATION OF 1,3,5-TRIALKYLBENZENE

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This invention relates to the nitration of aromatic compounds. More particularly it relates to the mononitration of 1,3,5-trialkylbenzenes and it is specifically concerned with the mononitration of 1,3,5-trimethylbenzene by mixtures of nitric and sulfuric acid, i.e. "mixed acid."

The mononitro derivative of a 1,3,5-trialkylbenzene, e.g. mesitylene, has been prepared by adding nitric acid to a solvent mixture of the hydrocarbon and acetic acid and/or acetic anhydride. This procedure has several disadvantages, viz.,

(1) The acetic acid and acetic anhydride are relatively costly.

(2) The large excess of nitric acid which must be employed is wasteful.

(3) The isolation of the reaction product, entailing the dilution of the reaction mass with a large quantity of water and subsequent ether extraction is laborious, hazardous, and costly.

(4) The disposal of acetic acid waste liquors constitutes a serious pollution problem; alternately the recovery of the acetic acid from the waste liquor is costly.

(5) The use of a mixture of nitric and acetic acids is hazardous.

(6) The process requires glass-lined or special alloy equipment, which, too, add to the cost of the procedure.

The foregoing disadvantages can be avoided to a large extent by employing a mixture of nitric and sulfuric acids as the nitrating reagent. However, the reaction of 1,3,5-trimethylbenzene and mixed acid is said to yield only polynitro products. (De La Mare and Ridd, "Aromatic Substitution, Nitration and Halogenation," Academic Press, Inc., New York, N.Y., 1959, p. 51.)

It is the principal object of the present invention to devise a method of nitrating a 1,3,5-trialkylbenzene to its corresponding mononitro-derivative utilizing a mixture of nitric and sulfuric acids, i.e. mixed acid.

This and other objects and advantages will be apparent from the following description of our invention.

We have made the surprising discovery that the mononitro-derivatives of 1,3,5-trialkylbenzenes can be prepared by a process which comprises adding a nitrating acid consisting essentially of nitric and sulfuric acids to a 1,3,5-trialkylbenzene and isolating from the reaction mixture mononitro 1,3,5-trialkylbenzene as the major product, the nitrating acid being employed in amount sufficient to provide from about 0.8 to about 1.2 moles of nitric acid per mole of the 1,3,5-trialkylbenzene and to provide during at least the major portion of the reaction a sulfuric acid concentration of from about 64% to about 80% calculated as described below.

The sulfuric acid concentration is determined by the following formula:

Sulfuric acid concentration, percent

$$=100\times\frac{Si+Sa}{Si+Sa+Wi+Wa+.285N}$$

wherein S*i* and W*i* are the weight of sulfuric acid and water respectively present in the reaction mixture before addition of the nitrating acid, S*a* and W*a* are the weights of sulfuric acid and water, respectively, added in the nitrating acid, N is the weight of nitric acid added. In determining the concentration as of any time, only the materials added up to that time are taken into account.

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The present invention affords mononitro-1,3,5-trialkylbenzenes in high yields, in the order of about from 60 to about 92% of the theoretical yield with formation of only minor amounts of the corresponding dinitro compounds.

The 1,3,5-trialkylbenzenes which can be mononitrated in accordance with the instant invention are those of which each alkyl group contains up to 3 carbon atoms; the following are examples of representative compounds:

1,3,5-trimethylbenzene (mesitylene)
1,3,5-triethylbenzene
1,3,5-tri-n-propylbenzene
1,3,5-tri-isopropylbenzene
1-methyl-3,5-diethylbenzene
1-methyl-3-ethyl-5-propylbenzene

The invention can be carried out by adding the nitrating acid to a 1,3,5-trialkylbenzene, preferably by adding the nitrating acid to a suspension of the 1,3,5-trialkylbenzene in a suitable diluent such as aqueous sulfuric acid or spent acid obtained as a "heel" from a preceding nitration.

The sulfuric acid concentration in the reaction mixture is maintained from about 64% to about 80% during at least a major portion of, and preferably throughout the entire reaction period in order to obtain a satisfactory conversion. Should the sulfuric acid concentration be below 64% oxidation and tar formation are extensive. If the sulfuric acid concentration is kept above 80% for an appreciable period, for example by inverse addition of the acid reagent and aromatic substrate, di- or trinitration occur to an objectional extent.

Preferably the sulfuric acid concentration should be maintained at from about 72% to about 76% during the entire reaction.

In the preferred embodiment of the instant invention, 17/65 mixed acid (containing 17% of HNO_3, 65% of H_2SO_4 and 18% of H_2O) is used. However any concentration of mixed acid (e.g. 29/57, 29/65 or 45½/54½) can be employed, if necessary, with a sufficient amount of diluent, e.g. aqueous sulfuric acid, to adjust the sulfuric acid concentration to the required level. Mixed acids are generally available as commercial products in many concentrations. It is possible, however, and in fact it may be desirable to prepare the mixed acid in situ, that is, by adding concentrated nitric acid to a suspension of the aromatic compound and sulfuric acid.

The amount of nitric acid employed should afford a mol ratio of nitric acid to 1,3,5-trialkylbenzene of at least about 0.8 and no more than about 1.2 to 1. Ratios lower than 0.8 will result in a low conversion of the aromatic substrate and ratios higher than 1.2 will result in exececssive dinitration. Preferably a ratio from about 0.9 to about 1.1 is employed.

The mixed acid is preferably added gradually to the reaction mixture, for example continuously or intermittently at a rate of about 0.1% to about 1% by weight of the mixed acid charge per minute. Preferably the reaction is continued after the addition is complete for a sufficient length of time to effect optimum production of the desired mononitro product, for example for about ½ hour.

The reaction temperature can be varied over the range of from about −10° C. to about 40° C. Lower reaction temperatures require expensive cooling and result in low conversion rates while high temperatures promote dinitration and oxidation. An especially good result is obtained when reaction temperatures are maintained between about +5° and 40° C. It is usually desirable to carry out a portion (say, ½ to ¾) of the mixed acid addition at one temperature, e.g. 5–10° C.) and to complete the addition and the reaction at a higher temperature (e.g. 24–40° C.). Higher temperatures may be utilized near or after completion of the reaction, for example during recovery of the product.

To minimize the formation of tarry by-products, it is desirable to carry out the nitration in the presence of a small amount, about 1.0 to about 1.5%, by weight of the aromatic substrate, of sulfamic acid or urea. Preferably, about 1.25% of sulfamic acid is employed. An especially good result is obtained by adding about ⅓ of this reagent, e.g. sulfamic acid, before addition of the mixed acid, about ⅓ after about 50% of the mixed acid has been added and about ⅓ after the additon of mixed acid is complete.

The equipment used in carrying out our invention may be of conventional design and such as is readily available. It can be fabricated of acid resistant material, i.e. stainless steel, cast iron, mild steel or glass. An efficient means for cooling the reaction vessel should be provided, as for example, a cooling jacket or immersed coil. An efficient agitator, temperature recorder and other usual appurtenances common to this type of equipment will be advantageous as will be obvious to those versed in the art.

The crude mononitro-1,3,5-trialkylbenzene can be readily isolated from the reaction mass by any one of several known methods. By one procedure, the reaction mass is maintained at a temperature about 5° C. above the melting point of the mononitro product until separation into two layers occurs. The upper organic layer containing the product is then separated from the lower acid layer by decantation.

Alternatively, the reaction mixture can be cooled to crystallize the mononitro product and the latter can be isolated by either filtration or centrifuging. Before carrying out either procedure, the crude reaction mass can, if desired, be diluted with a large quantity of water.

The crude mononitro-1,3,5-trialkylbenzene obtained is generally suitable for use without further treatment. However, if desired, the crude product can be purified by washing, crystallization, distillation or other suitable method.

The following examples illustrate the process of our invention. Parts and percentages are by weight and temperatures are given in degrees centigrade.

EXAMPLE 1

A mixture of 70% sulfuric acid (200 parts) and mesitylene (240 parts, 2 mols) was vigorously agitated and cooled to 5°. To this 17/65 mixed acid (740 parts) containing 17% nitric acid (corresponding to 2 mols of nitric acid), 65% sulfuric acid and 18% water was added over a period of 1½ hours. During the addition the temperature of the reaction mass was maintained at 5°–10°. After the addition had been completed, the reaction mixture was stirred for an additional ½ hour while the reaction mixture temperature was allowed to rise to about 30°. In this instance the sulfuric acid concentration, calculated as heretofore set forth, varied from about 70 at the onset of the reaction to about 73 at the end thereof. The reaction mixture was heated to 40° and allowed to stand at this temperature until stratification occurred. The lower layer of spent acid was separated and discarded. The upper organic layer consisted of crude nitromesitylene (320 parts, 97% of theory) which was converted to mesidine by the Béchamp reduction. Hydrochloric acid (35 parts, 20° Bé.) was added to an agitated mixture of the crude product, water (200 parts) and iron powder (35 parts, 60 mesh). The reaction mass was heated to reflux and additional iron powder (315 parts) was charged over a period of one hour. On completion of the addition the reaction mixture was refluxed for eight hours and calcium hydroxide (30 parts) was added. The reaction mass was steam distilled and the distillate which consisted of an upper oily layer and a lower aqueous layer was collected in a receiver which permitted the continuous return of the latter phase to the still. The oily layer (237 parts) of

the distillate was separated and distilled under diminished pressure. Mesidine (213.4 parts, 64.5% yield based on mesitylene) distilled at 101–107° (10 mm.).

EXAMPLE 2

The nitration of mesitylene was carried out substantially as described in Example 1 except that the reduction of nitromesitylene to mesidine was omitted and the 17/65 mixed acid was added in increments so as to give successive mol ratios of nitric acid to mesitylene of 0.50, 0.75, 0.85, 0.95, 1.00 and 1.05. After each increment of mixed acid had been added, a sample was withdrawn from the reaction mass, washed successively with water, aqueous sodium carbonate, and water; dried and analyzed by vapor phase chromatography. The results of this experiment are presented in Table I.

Table I

Mol ratio of nitric acid to mesitylene	Composition of nitration product [1]		
	Percent mesitylene	Percent mononitro mesitylene	Percent dinitro mesitylene
0.5	62.6	33.3	1.1
0.75	38.7	55.9	2.1
0.85	15.5	77.9	2.6
0.95	11.2	81.7	3.4
1.00	2.6	90.0	3.4
1.05	0.1	91.6	3.5

[1] Unidentified impurities in the product account for the difference between the sum of the three components analyzed for and 100%. The results relate only to the volatile fraction of product.

EXAMPLE 3

Over a period of one hour 17/65 mixed acid (463 parts) which afforded sulfuric acid concentration (calculated as hereinabove set forth) of 74 throughout the reaction and contained 77.7 parts (1.2 mol) of nitric acid was added to a vigorously agitated mixture of mesitylene (150 parts, 1.25 mol) and sulfamic acid (0.5 part) which had been cooled to 5°. 0.5 part portions of sulfamic acid were added after 50% and 100% of the mixed acid had been charged. During the addition of the first 75% of the mixed acid the temperature of the reaction mixture was maintained at 5–10°; during the addition of the final 25% of mixed acid the temperature was allowed to rise to 25–30°. On completion of the addition, the reaction mass was heated to 40° over a period of one-half hour and allowed to stand at that temperature until stratification occurred. The upper organic layer which consisted of crude nitromesitylene (201 parts, 98% yield) was separated and reduced to mesidine (58% yield based on mesitylene) substantially as described in Example 1.

EXAMPLES 4–12

The procedure of Example 3 was repeated in a number of experiments wherein the composition of the mixed acid was varied so as to afford different sulfuric acid concentrations. The mol ratio of nitric acid is mesitylene was maintained at 1:1. The results of these experiments are given in Table II.

Table II

Example	Sulfuric acid concentration	Percent yield crude nitromesitylene	Percent yield mesidine (based on mesitylene)
4	62	[1] 0	----------
5	64	80	----------
6	66	83	----------
7	68	88	49
8	70	84	49
9	72	94	52
10	76	100	64
11	78	99	51
12	80	99	----------

[1] The entire product was an intractable tar.

EXAMPLE 13

Over a three hour period, 17/65 mixed acid (1480 parts) containing 252 parts (4 mols) of nitric acid was added to an agitated mixture of mesitylene (480 parts, 4 mols) and sulfamic acid (4 parts) which had been cooled to 5°. During the addition of the first 75% of the mixed acid, the temperature of the reaction mixture was maintained at 5–10°; during the addition of the final 25% of the mixed acid the temperature of the reaction mixture was held at 25–30°. On completion of the addition, 2 parts of sulfamic acid were added and the reaction mixture was agitated for ½ hour at 25–30°. The mixture was heated to 50° and allowed to stratify. The upper organic layer consisting of crude nitromesitylene (97.5% yield, setting point 29.9°) was separated from the lower spent acid layer. When a portion of the latter phase was drowned in water, the resulting solution was only slightly turbid, indicating the substantial absence of tarry by-products.

EXAMPLE 14

The nitration of mesitylene was carried out as described in Example 13 except that the sulfamic acid was omitted. Both the crude nitromesitylene and the spent acid layer were darker in color than the corresponding products in Example 13. When a portion of the spent acid layer was drowned in water, the resulting solution was turbid due to the presence of tarry by-products formed in the nitration.

EXAMPLE 15

The nitration of mesitylene was carried out substantially as described in Example 1 except that the mixed acid was added over a period of about 4 hours. From 120 parts of mesitylene 163 parts (98.6% of theory) of crude nitromesitylene (setting point 35°) were obtained.

The crude product was mixed with water (300 parts) and adjusted to a pH of about 8 by the addition of sodium carbonate. "Nacconol" NR (an alkylsodium sulfonate, 0.2 part) and "Tween" 60 (a polyoxyalkylene derivative of sorbitan monostearate, 0.3 part) were added to the mixture which was heated to 50° and cooled with vigorous agitation to 5°. The crystalline solid which separated was recovered by filtration, washed with cold water, dried and yielded 130 parts (78.7%) mononitromesitylene (setting point, 40.6°).

EXAMPLE 16

Mesitylene (60 parts, 0.5 mol) was added to a mixture of 17/65 mixed acid (370 parts, containing 1 mol of nitric acid) and of 70% sulfuric acid (100 parts) maintained at 8–15°. The crystalline solid which formed as the mesitylene was added was recovered by filtration, washed with water and dried. A yield of 103 parts (98%) of dinitromesitylene (M.P. 83–85°) was obtained.

EXAMPLE 17

Mesitylene (240 parts, 2 mols) was nitrated essentially as described in Example 1 except that 29/65 mixed acid (435 parts) containing 2 mols of nitric acid was used as the nitrating reagent. In this reaction the sulphuric acid concentration varied from 70 at the onset of the reaction to 77.7 at the end thereof. A good yield of crude mononitromesitylene was obtained.

EXAMPLE 18

Sulfamic acid (15 parts) was added to mesitylene (3605 parts, 30 mols) at −2°. Over a period of eight hours 10,839 parts of 17.35/65 mixed acid containing 1889 parts (30 mols) of nitric acid were charged. Sulfamic acid (15 parts) was charged after 5420 parts of mixed acid had been added. On completion of the mixed acid addition, additional sulfamic acid (16 parts) was added to the reaction mixture. During the addition of the first 75% of the mixed acid, the temperature of the reaction mass was maintained at 0–5°; during the addition of final 25% of mixed acid, the temperature was allowed to rise to 18°. Over a period of one hour the reaction mass was heated to 40° and maintained at that temperature for one hour. After standing for 12 hours, the reaction mass stratified. The organic layer which was separated consisted of crude nitrated product (4793 parts, 97% yield) and had a setting point of 34°.

It can thus be seen that a process has been devised for mononitrating 1,3,5-trialkylbenzenes utilizing mixtures of nitric and sulfuric acid and that this process is readily adapted to the commercial production of mononitro-1,3,5-trialkylbenzenes. It is to be understood that the above examples, although including the preferred embodiments of our invention, are given for the purpose of illustration, and that considerable variation can be made without departing from the scope and spirit of the invention. For example, the invention may be carried out continuously rather than batchwise.

The procedure of our invention possesses several advantages over the processes of the prior art of which the following are the more important:

(1) *Simplicity.*—No organic solvent is required and hence the laborious and often expensive treatments necessitated by use of such solvents are avoided. The reagents employed in the present process are easily handled and present no unusual hazard to personnel or equipment.

(2) *Economy.*—The reagents used are readily available and of moderate cost. The process can be operated on either a batch or continuous basis.

(3) *Efficiency.*—The present process which is effected with a minimum excess of reagents is productive of excellent yields in the order of 60% to 97% of theory and of high quality product, the product being generally suitable for use without further purification.

We claim:

1. A process for preparing a mononitro 1,3,5-trialkylbenzene containing from 1 to 3 carbon atoms in the alkyl groups which comprises nitrating the corresponding 1,3,5-trialkylbenzene in the presence of sufficient sulfuric acid to provide a sulfuric acid concentration of from 64% to 80% calculated by the following formula:

Sulfuric acid concentration, percent

$$=100\times\frac{Si+Sa}{Si+Sa+Wi+Wa+.285N}$$

in which S*i* and W*i* are the weights of the sulfuric acid and water initially present in the reaction mixture, S*a* and W*a* are the weights of sulfuric acid and water thereafter added to the reaction mixture, and N is the weight of nitric acid added to the reaction mixture.

2. A process for preparing mononitromesitylene which comprises nitrating mesitylene in the presence of sufficient sulfuric acid to provide a sulfuric acid concentration of from 64% to 80% calculated by the following formula

Sulfuric acid concentration, percent

$$=100\times\frac{Si+Sa}{Si+Sa+Wi+Wa+.285N}$$

in which S*i* and W*i* are the weights of the sulfuric acid and water initially present in the reaction mixture, S*a* and W*a* are the weights of sulfuric acid and water thereafter added to the reaction mixture, and N is the weight of nitric acid added to the reaction mixture.

3. A process for preparing a mononitro 1,3,5-trialkylbenzene which comprises adding to 1,3,5-trialkylbenzene containing from 1 to 3 carbon atoms in the alkyl groups, nitric acid and sulfuric acid, maintaining the sulfuric acid concentration in the reaction mixture within the range of 64% to 80% calculated by the following formula:

Sulfuric acid concentration, percent

$$=100\times\frac{Si+Sa}{Si+Sa+Wi+Wa+.285N}$$

in which Si and Wi are the weights of the sulfuric acid and water initially present in the reaction mixture, Sa and Wa are the weights of sulfuric acid and water thereafter added to the reaction mixture, and N is the weight of nitric acid added to the reaction mixture, continuing addition of the nitric acid until from 0.8 to 1.2 moles of nitric acid per mole of the hydrocarbon have been added, and maintaining the temperature of the reaction mixture within the range of −10° C. to 40° C. during at least the major portion of the reaction.

4. A process for preparing mononitromesitylene which comprises adding to mesitylene nitric acid and sulfuric acid, maintaining the sulfuric acid concentration in the reaction mixture within the range of 64% to 80% calculated by the following formula:

Sulfuric acid concentration, percent

$$=100\times\frac{Si+Sa}{Si+Sa+Wi+Wa+.285N}$$

in which Si and Wi are the weights of the sulfuric acid and water initially present in the reaction mixture, Sa and Wa are the weights of sulfuric acid and water thereafter added to the reaction mixture, continuing addition of the nitric acid until from 0.8 to 1.2 moles of nitric acid per mole of mesitylene have been added, and maintaining the temperature of the reaction mixture within the range of −10° C. to 40° C. during at least the major portion of the reaction.

5. The process as specified in claim 4 in which the sulfuric acid concentration is maintained within the range of 72% to 76% during at least a major portion of the reaction.

6. A process as specified in claim 4 in which the reaction is carried out in the presence of a member of the group consisting of sulfamic acid and urea.

7. A process as defined in claim 4 in which nitric acid is added to the reaction mixture gradually as a mixture of nitric acid and sulfuric acid.

8. A process as defined in claim 7 in which the reaction is initially conducted at temperature of below 10° C. and the temperature is thereafter raised to within the range of 25 to 40° C.

9. A process of producing mononitromesitylene which comprises adding to a mixture of sulfuric acid and mesitylene, mixed nitrating acid containing about 17% of nitric acid and 65% of sulfuric and 18% of water gradually at the rate of about 0.1% to about 1% of the mixed acid charged per minute, continuing addition of mixed acid until from 0.9 to 1.1 mole of nitric acid per mole of mesitylene has been added to the reaction mixture, maintaining the sulfuric acid concentration of the reaction mixture within the range of 72% to 76% as calculated by the following formula.

Sulfuric acid concentration, percent

$$=100\times\frac{Si+Sa}{Si+Sa+Wi+Wa+.285N}$$

in which Si and Wi are the weights of the sulfuric acid and water initially present in the reaction mixture, Sa and Wa are the weights of sulfuric acid and water thereafter added to the reaction mixture, and N is the weight of nitric acid added to the reaction mixture, maintaining the temperature of the reaction mixture below 10° C. during the initial stages of the reaction and thereafter raising temperature of reaction mixture to within the range of 25° to 40° C., carrying out the reaction in the presence of sulfamic acid in amount not exceeding about 1.5% by weight of the mesitylene, and recovering mononitromesitylene from the reaction mixture.

No references cited.