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ELECTROLYSIS OF PRIMARY NITROALKANES

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7 Claims. (Cl. 204—79)

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This invention relates to a process for the preparation of nitroolefins and polynitro compounds, and more particularly to the preparation of such compounds by the oxidative electrolysis of salts of primary aci-nitroalkanes containing more than one carbon atom.

Electrolytic methods of the reductive type have been employed heretofore to treat and reduce nitro compounds either partially or completely, carrying out this step at the cathode or negative pole of the electrolytic cell. Oxidative reactions, on the other hand, that is, reactions carried out at the anode or positive pole have not been generally utilized, largely because the mechanism of the reactions which might take place at this pole is not at all well understood. Theories recently advanced attempting to explain oxidative reactions are of limited practical value in describing what takes place at the anode, and it still remains a matter of uncertainty as to what products, if any, will be obtained through the electrolysis of any given material at the anode pole, and why the reactions, if any, take place as they do.

An object of the present invention is to provide a method for the production of valuable products through the oxidative electrolysis of salts of primary aci-nitroalkanes containing more than one carbon atom.

A further object is to provide a method for the preparation of a mixture of nitroolefins and polynitro compounds.

Another object is to provide a method for the preparation of nitroolefins from salts of primary aci-nitroalkanes containing from two to eight carbon atoms.

A still further object is to provide a method for the preparation of polynitro compounds having the nitro groups on adjacent carbon atoms.

Other objects will be apparent from the specification and claims.

I have found that if the lower primary nitroalkanes in the form of the alkaline salts of the aci-nitroalkane are subjected to electrolysis at the anode pole of an electrolytic cell, under conditions described hereinafter, nitroolefins and polynitro compounds in which the nitro groups are located on adjacent carbon atoms are formed.

The nitroolefins produced according to my process are mononitroolefins having twice the number of carbon atoms as the original starting nitroalkane employed. The polynitro compounds produced are compounds containing multiples of the number of carbon atoms of the nitroalkane treated, primarily the dinitro compounds together with smaller quantities of compounds which appear to be trinitro and higher nitrated compounds of the same type. In the case of the polynitro compounds, the nitro groups are located on different but adjacent carbon atoms. These products can readily be separated by fractional distillation in the case of liquid products or by crystallization in the case of the solid compounds.

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The nitroalkanes employed as starting materials in carrying out my invention have the following general formula:

$$R—CH_2—NO_2$$

wherein R represents an alkyl group having from 1 to 7 carbon atoms.

The nitroolefins and dinitro compounds prepared in accordance with my invention have the following formulas, respectively:

$$R—\underset{\displaystyle NO_2}{\overset{|}{C}}=CH—R$$

and

$$R—\underset{\displaystyle NO_2}{\overset{|}{CH}}—\underset{\displaystyle NO_2}{\overset{|}{CH}}—R$$

wherein R represents an alkyl group having from 1 to 7 carbon atoms.

In practicing my invention, I prepare an electrolytic cell comprising positive and negative poles immersed in anolyte and catholyte solutions respectively, separated from each other by a semi-porous diaphragm. As an anode or positive pole, I may utilize any suitable conductor, preferably one which is inert to the anolyte solution with respect to corrosion, and for this purpose platinum has proved satisfactory and lead can be used although the fact that some corrosion ensues renders it less effective than the platinum. The cathode or negative pole is less critical because corrosion rarely occurs at this pole because under the conditions described, reduction and not oxidation is the usual reaction at this pole. Accordingly, copper or other suitable conductor, is satisfactory as a cathode material.

As the anolyte solution, I employ in solution a salt of the aci-nitroalkane to be electrolyzed. For this purpose the alkali salts such as sodium, potassium, and the like are preferable because of their generally high solubility. The aci-nitroalkane salt may be prepared in any known manner, a suitable procedure being to add the nitroalkane, slowly with agitation to a solution of the salt forming material such as an alkali metal hydroxide such as sodium hydroxide at a relatively ele-

vated temperature, for example, between about 75 to 85° C. If the nitroalkane is one which does not form a salt readily, I find it convenient to first prepare an alcoholic solution of the salt forming reactant such as sodium alcoholate, and add the nitroalkane thereto. After removing the alcohol, the salt may be dissolved in water or suitable solvent, and the solution then used as the anolyte material. An aqueous solution of the aci-nitroalkane salt of the first nitroalkane, i. e., nitromethane, cannot be prepared by either expedient, as this nitroalkane goes immediately to the methazonic acid salt in the presence of aqueous alkali as is well known. A solution of the aci-nitroalkane salt as such, affords a satisfactory anolyte material for my electrolysis, but I have found that if an excess of base is added, higher yields of product are obtained, and I have found that optimum yields are obtained when the excess of base is substantial, for example, from ½ to 1½ moles in excess of that required to convert the aci-nitroalkane to the alkali salt. In other words, in preparing my anolyte solution I prefer to utilize between 1½ to 2½ moles of base per mole of nitroalkane.

As the catholyte solution, I may use any suitable electrolyte, preferably an alkaline material containing the same metal radical as used in forming the alkaline salt of the aci-nitroalkane. The use of an identical alkali metal is simply a matter of convenience to prevent the possibility of conflicting reactions by the migration of metal ions from the anolyte to the catholyte. Thus, when the sodium salt of an aci-nitroalkane is employed as anolyte, the sodium ion migrates to the catholyte and as a result of action at the cathode, sodium hydroxide is formed. If the original catholyte is sodium hydroxide solution, this merely increases its concentration. Solutions of other electrolytes may be employed as catholytes however.

After the anolyte solution, prepared as above described, has been cooled, preferably to room temperature, it is placed in the anode compartment of an electrolytic cell and an electric current is passed through the cell at a suitable current density.

The current densities which can be used vary widely, even relatively low values producing satisfactory results, and also higher values than those commercially convenient give a satisfactory production of the desired products, and these values do not appear to be critical. The higher current densities have the advantage of reducing the time for electrolysis and thus increasing the capacity of a given cell. On the other hand, high current densities increase the voltage requirement and require more cooling to obtain optimum yields of desired products. Where the current density is defined as amperes current passed per square centimeter of active electrode surface, I preferably employ a current density of about .03 to .11, representing an average current of about 1.2 to 4.5 amperes for an anode having an active area of about forty square centimeters.

The time of electrolysis will vary with the current density, and the quantity of aci-nitroalkane in relation to the area of the anode and likewise the yield of product at a given current will vary with the time of electrolysis. In any case, the amount of current theoretically necessary to effect the desired conversions should be passed, namely, at least one faraday per mole of starting material and it is usually advantageous to pass somewhat more than the theoretical amount, usually between one and two faradays per mole of nitroalkane used.

The temperature during electrolysis should be maintained relatively low, the particular temperature depending to some extent on the aci-nitroalkane employed, the lower members requiring somewhat lower temperatures for optimum yields than the higher members. Electrolysis will of course occur at higher temperatures, but at elevated temperatures, yields of desired products are lower, particularly in the case of the lower nitroalkanes. Since the electrolysis reaction tends to increase the temperature, cooling will usually be resorted to, for example, by means of a water or ice bath or other suitable device. I have found that adequate yields are obtained when the temperature is maintained at room temperature or anywhere between about 10 and 35° C., or somewhat higher in the case of the higher aci-nitroalkanes.

As the reaction products of the electrolysis are formed, they will, in most cases separate from the anolyte solution as immiscible materials either rising to the top or settling to the bottom of the cell depending on their densities relative to that of the anolyte solution. Care should be taken to facilitate this separation, and particularly to avoid as far as possible too intimate contact between the products of the electrolysis and the remaining anolyte. This is desirable as the end products may react again with the anolyte to form undesired products with consequent reduction in the yield. Thus, excessive turbulence of the solution is undesirable and violent stirring and mixing or the like during electrolysis are to be avoided. However, some gentle movement of the material is desirable in order that successive quantities of the anolyte may come within the range of influence of the anode to there react to form the desired product. In view of the ready separation of the reaction products as described above, I may carry out my process continuously if desired, i. e., with continuous addition of fresh anolyte, and continuous separation of reaction product. In the case of the lower nitroalkanes, the density of the anolyte can be adjusted so that by proper choice of concentration the crude end products have specific gravities higher or lower as the case may be than that of the aci-nitroalkane salt solution used as anolyte, and so will either rise to the top of the cell or sink to the bottom, and can be continuously removed by overflow or other convenient means.

The reaction occurring at the anode is not completely understood, but from the results obtained, it appears that the reaction is essentially an ionization and coupling of two or more ions of the primary nitroalkane, producing mononitroolefins and saturated polynitro compounds.

The process appears to be applicable to compounds of the class described, having two or more carbon atoms, and is conveniently operable with lower aci-nitroalkane salts having from two to eight carbon atoms. The first member of the alkane series, namely, nitromethane, although it may be regarded as a primary nitro compound, behaves in an anomalous manner going over to the methazonic salt upon addition of aqueous alkali.

Examples of primary nitroalkanes which yield the type of products described, when subjected to oxidative electrolysis according to my process are nitroethane, 1-nitropropane, 1-nitrobutane,

1-nitropentane, 1-nitrohexane, 1-nitroheptane, and 1-nitrooctane. From nitroethane I obtain primarily 2-nitro-2-butene and 2,3-dinitrobutane; from 1-nitropropane I obtain 3-nitro-3-hexene, and 3,4-dinitrohexane as major constituents and a smaller amount of a residue which was not definitely identified. From 1-nitrobutane I obtain 4-nitrooctene, 4,5-dinitrooctane and a small unidentified residue. From the higher carbon containing nitroalkanes, analogous products are obtained. Of these products, both the dinitro compounds and the nitroolefins are valuable chemical entities and because of their reactive nature, the nitroolefins serve as a starting point for many valuable syntheses, including that resulting from the reaction of the nitroolefins with salts of malonic acid esters described in my U. S. Patent No. 2,431,451, granted November 25, 1945.

The following examples are illustrative of my invention:

EXAMPLE I

Electrolysis of sodium aci-1-nitropropane

A solution containing 80 parts by weight of sodium hydroxide, 100 parts of 1-nitropropane, and 200 parts of water was placed in an unglazed porcelain diaphragm container, 5 inches (12.7 cm.) high and 3 inches (7.6 cm.) in diameter. A platinum gauze cylinder 1⅜ inches (3.5 cm.) in diameter and 2 inches (5.1 cm.) high was immersed in the diaphragm cup to serve as the anode. A cathode of six feet of No. 16 copper wire was coiled around the the outside of the diaphragm and the diaphragm was placed in an 800 cc. beaker. The catholyte was 25% sodium hydroxide solution, 250 parts.

Electrolysis was carried out for 22 hours, 2.5 amperes passing at 4.5 to 5.5 volts. The temperature varied from 38 to 48° C. The anodic current density was approximately 0.045 amp./cm.^{2}.

The final anolyte consisted of an oil and water layer. The oil layer of the anolyte was separated and washed with water, and resulted in a quantity equal to 30.4 parts by weight.

Distillation of the oil layer from a Claisen flask gave the following fractions:

1. 35–73° (3 mm.) ——— 50% of original oil
2. 73–115° (2–3 mm.) ——— 20.2% of original oil
3. Residue ——— 17.6% of original oil

Fractions 1 and 2 were refractionated through an eight inch modified Widmer column.

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1. 69–74° (10 mm.)	8.3
2. 56–90° (2 mm.)	4.0
3. 90–95° (2 mm.)	3.8
4. Residue	0.4

Fraction 1 was analyzed and the properties were compared with 3-nitro-3-hexene prepared by a different method.

	Fraction 1	3-Nitro-3-hexene
B.P. (10 mm.) degrees	69–74	66–69
N (Theo 10.93)	11.29	11.04
n_D^{20}	1.4543	1.4580
$D\frac{20°}{20°}$	0.9998	0.9832

Fraction 1, after redistillation through a packed column had a density of 0.9833. The purified material was also characterized by comparing crystalline derivatives thereof with the derivatives of 3-nitro-3-hexene prepared according to methods described in the literature.

Fraction 3, boiling at 90–95° at 2 mm., had the following analysis; indicating a somewhat impure 3,4-dinitrohexane.

	Found	Theory for 3,4-Dinitrohexane
Nitrogen	14.44	15.9
n_D^{20}	1.4603	
$D\frac{20°}{20°}$	1.1372	

The product was further qualitatively identified as 3,4-dinitrohexane by the nickel dimethylglyoxime test, as described in the literature which involves reduction of the dinitro compound followed by air oxidation in the presence of a nickel salt and aqueous ammonia. This test converted the 3,4-dinitrohexane into the reddish nickel dimethylglyoxime which in turn was converted to the free dimethylglyoxime whose melting point agreed with that found in the literature. The purified material was further characterized by comparing crystalline derivatives thereof with the derivatives of 3,4-dinitrohexane prepared according to the methods described in the literature.

The residue from the first distillation was a dark viscous liquid which could not be made to crystallize. It contained 12.63% nitrogen compared to 15.95% nitrogen for 3,4,5-trinitro-4-ethylheptane.

EXAMPLE II

Electrolysis of sodium aci-1-nitropropane

To a solution of 80 parts by weight of sodium hydroxide in 200–250 parts of water, 100 parts by weight of technical 1-nitropropane were added gradually with vigorous stirring at 75–85° C. After all the 1-nitropropane had dissolved, to form the sodium salt of aci-1-nitropropane, the solution was cooled to room temperature and placed in the anode compartment of the electrolytic cell. The anode or positive pole, a piece of platinum foil, having an area of 40 square centimeters was suspended in the solution. A copper wire spiral, the cathode or negative pole, was immersed in a 25% aqueous sodium hydroxide solution contained in an Alundum vessel and the vessel in turn was placed in the cell, immersed in the anolyte solution. An electric current was then passed through the cell for about 24 hours at an average of about 2.0–2.5 amperes and 5 volts at 30–35° C. (Current density .05 to .06). This electrolysis yielded about 50 parts by weight of yellow oil which floated on the surface of the anolyte and was recovered by the aid of a separatory funnel. This oil was distilled under vacuum and yielded the following:

	Yield, Per Cent of Anode Oil
(1) 3-nitro-3-hexene, a low boiling fraction distilling at about 50° C. at 4 mm. pressure	45–55
(2) 3,4-dinitrohexane, a high boiling fraction distilling at about 90° C. at 1 mm. pressure	25–30
(3) Residue containing higher boiling nitro compounds	10–15

EXAMPLE III

Electrolysis of sodium aci-1-nitrobutane

Sodium aci-1-nitrobutane was electrolyzed as described under Example II and yielded about 65 parts by weight of anode oil from 100 parts of 1-nitrobutane. Upon distillation, this yielded:

	Yield, Per Cent of Anode Oil
(1) 4-nitrooctene, distilling at about 58–69° C. at 2 mm. pressure	35
(2) 4,5-dinitrooctane, distilling at about 109–115° C. at 2 mm. pressure	35
(3) Residue	10

EXAMPLE IV

Electrolysis of Sodium Aci-Nitroethane

An anolyte solution was prepared by adding 50 parts by weight of redistilled nitroethane to 26.6 parts of sodium hydroxide in 125 parts of water during a period of three minutes with vigorous stirring at 54 to 70° C. The mixture was stirred two minutes longer at about 67° C., then cooled to 30° C. The anolyte thus prepared was placed in an electrolytic cell similar to that used in the foregoing examples and the cell was cooled by an ice bath during the ensuing electrolysis. An electric current was passed through the cell and electrolysis was continued for 11 hours at 15 to 22° C., at an average of about 7.5 volts, 1.5 amperes, representing a current density of about .0375 ampere/sq. cm. The final product was 6.5 parts by weight of clear liquid

$$D_4^{25}=1.28$$

and was strongly lachrymatory. A portion of the oil was distilled and a fraction obtained between 72° C. at 25 millimeters and 78° C. at 23 millimeters corresponding to impure 2-nitro-2-butene, which was characterized by comparing its boiling point and other physical properties with the properties described in the literature. Very little additional distillate was obtained until the temperature was raised to 95° C. at one millimeter pressure when a fraction was obtained from which crystals were obtained having a melting point of 108°C. indicating an isomeric form of 2,3-dinitrobutane. The presence of 2,3-dinitrobutane in the anode oil was confirmed by forming the red nickel dimethylglyoxime precipitate as described in the literature.

A primary advantage of my invention is that it provides a simple, straightforward method for producing nitroolefins and polynitroalkanes of the type described directly from nitroalkanes without intermediate chemical substitution processes which have heretofore been considered essential.

While the above description points out the preferred embodiments of my invention, it will be understood that departures may be made therefrom within the scope of the specification and claims.

What is claimed is:

1. In the preparation of a mixture of nitroolefins and dinitroalkanes by electrolysis in an electrolytic cell having an inert anode and being separated into an anode compartment and a cathode compartment by means of a porous diaphragm, the process which comprises introducing

into the anode compartment of said cell in contact with said anode an aqueous solution of the alkali metal salt of an aci-1-nitrolkane containing from two to eight carbon atoms, passing an electric current through said cell from the anode to the cathode at a current density of from about 0.03 to 0.11 ampere per square centimeter while maintaining the temperature within the range of about 10° to 48° C. until conversion to a mixture of nitroolefin and dinitroalkane has occurred, and recovering the resulting nitroolefin and dinitroalkane from the anolyte.

2. The process of claim 1 wherein said alkali metal nitroalkane salt solution contains an excess over molecular proportions of an alkali metal base amounting to from about ½ to 1½ moles of base per mole of said nitroalkane.

3. The process of claim 1 wherein from about 1 to 2 faradays are passed through said cell per mole of nitroalkane salt.

4. The process of claim 1 wherein the primary nitroalkane salt subjected to electrolysis is an alkali metal salt of aci-1-nitropropane.

5. A process of claim 1 wherein the primary nitroalkane salt subjected to electrolysis is an alkali metal salt of aci-1-nitrobutane.

6. The process of claim 1 wherein the primary nitroalkane salt subjected to electrolysis is an alkali metal salt of aci-1-nitroethane.

7. In the preparation of a mixture of nitroolefins and dinitro alkanes by electrolysis in an electrolytic cell having an inert anode and being separated into an anode compartment and a cathode compartment by means of a porous diaphragm, the process which comprises adding a primary nitroalkane containing from 2 to 8 carbon atoms to an aqueous solution of a caustic alkali, said solution containing from about 1½ to 2½ moles of alkali per mole of nitroalkane added, introducing the resulting solution of nitroalkane salt into the anode compartment of said electrolytic cell in contact with said anode, passing an electric current at a density of about 0.03 to 0.11 ampere per square centimeter through said cell from the anode to the cathode while maintaining the temperature within the range of about 10° to 35° C. and until from about 1 to 2 faradays are passed through the cell per mole of nitroalkane salt, and recovering the resulting mono- and di-nitro compounds from the anolyte.

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