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PROCESS FOR PREPARING CARBOXYLIC ACIDS BY IRRADIATION

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This invention is concerned with a new process for synthesizing carboxylic acids.

Heretofore numerous methods of synthesizing carboxylic acids have been proposed. Most of these involve chemical reactions that are somewhat complicated and, for various reasons, become difficult to accomplish as the molecular weight of the acid produced increases. In particular, so far as known there has been proposed no simple and general way of forming a carboxylic acid by direct addition of carbon dioxide to a hydrocarbon.

An object of the present invention is, consequently, provision of a novel and useful method of preparing carboxylic acids.

Another object is provision of a method of preparing carboxylic acids general to a large number of such acids.

A specific object is provision of a method of synthesizing carboxylic acids by direct addition of carbon dioxide to a hydrocarbon.

The above-mentioned and yet further objects are achieved in accordance with this invention by a process in which a mixture of carbon dioxide and an organic compound containing at least one C—H aliphatic linkage is subjected to ionizing radiation having an energy above 50 e.v. (electron volts), carbon dioxide being maintained in the reaction mixture throughout the time of radiation. The resultant carboxylated material is then separated from the reaction mixture.

For the purposes of this specification, the term "ionizing radiation" will be restricted to (1) accelerated electrons and (2) photons with a maximum associated wave length in the X-ray portion of the electromagnetic spectrum.

By ionizing radiation in the form of electrons is meant a beam of accelerated electrons which impinges upon the mixture of carbon dioxide and the organic compound. The electrons may be accelerated by means of a voltage gradient of at least 50 volts by such devices as a resonant cavity accelerator, a Van de Graaff accelerator, a betatron, or the like. Suitable accelerated electrons may also be obtained as beta radiation from radioactive isotopes, such as C^{14}, P^{32}, Sr^{90}, tritium and the like.

By ionizing radiation in the form of photons is meant electromagnetic radiation of the type commonly known as X-rays and gamma rays. X-rays are formed when electrons of appropriate energy bombard other forms of matter, particularly metals. Hence, X-rays are usually present in practical situations where accelerated electrons are employed. X-rays may be generated in high yields by bombarding a metal target, such as gold or tungsten, with high energy electrons. Gamma rays represent the same form of electromagnetic radiation as X-rays and differ primarily in that their source is a radioactive substance, for example, cobalt 60.

Two types of radiation that might be included in the term "ionizing radiation" are specifically excluded by the definitions given above. These are alpha particles and a silent electric discharge. These have been shown to yield largely oxidation products of hydrocarbons when utilized to irradiate mixtures of the latter with carbon dioxide.

Thus Berthelot, "Essai de Mechanique Chemique," Dunod, Paris, vol. II, pp. 382–3 (1879), found that the silent discharge applied to mixtures of methane and carbon dioxide yielded an insoluble, caramel-like product. Lind and Bardwell, J. Am. Chem. Soc. 48, 2349 (1926), produced a polymer of formaldehyde by irradiating a similar mixture with alpha particles from radon. To avoid contamination of the desired carboxylic acids, α-particles and the silent discharge should not be employed in this invention.

Organic compounds suitable for carboxylation with carbon dioxide according to the present invention are those containing at least one aliphatic C—H group, the remaining three bonds of the carbon atom being attached to separate atoms. With all such compounds, the process produces the reaction:

$$-\overset{|}{\underset{|}{C}}-H+CO_2 \longrightarrow -\overset{|}{\underset{|}{C}}-COOH$$

The presence of certain functional groups in the molecule of the organic compound containing the C—H group may lead to side reactions which lower the yield of carboxylic acid. Accordingly, the saturated aliphatic and aryl aliphatic hydrocarbons represent the most preferred group of organic compounds for use in this invention since they are free of such side reactions. Another group preferred for the same reason comprises the aliphatic and aryl aliphatic alcohols and ethers. A third preferred group is the aliphatic and aryl aliphatic amines which yield amino acids.

With some organic compounds the yields of the expected carboxylated derivatives are low because of the simultaneous formation of other acidic by-products. Accordingly, these compounds are less preferred as starting materials. Thus, ketones yield major amounts of carboxyl derivatives of their cleavage products (i.e., acetone yields primarily acetic acid) and C—H compounds which are otherwise perhalogenated give low yields of the corresponding acid (i.e., chloroform gives very low yields of trichloroacetic acid along with unstable by-products which decompose to give off hydrogen chloride). Fully aromatic compounds, such as benzene, are not operable in the process of this invention.

There are many established routes for the preparation of common acids, such as acetic, propionic, butyric and isobutyric acids, with which the present process can compete economically only when cheap sources of suitable ionizing radiation are available. In the preparation of carboxylic acids containing five and more carbon atoms my process is more practicable than other processes. Aliphatic hydrocarbons, alcohols, ethers and amines containing four or more carbon atoms, consequently, represent a particularly preferred class of starting materials for this invention.

The carbon dioxide and the C—H compound must be in intimate contact during the time of irradiation. The organic compound should, therefore, preferably be a liquid or a gas at the temperature of irradiation in order to facilitate mixing of the reactants. When the organic compound is a liquid, the carbon dioxide may be mechanically dispersed therein during irradiation. Since the solubility of carbon dioxide in most organic liquids increases with pressure, superatmospheric pressure is sometimes preferred. This practice permits the irradiation of a solution of carbon dioxide in a liquid organic compound without the presence of a separate gas phase. When the organic compound is a gas at the irradiation temperature, the use of superatmospheric pressures on the mixture of organic compound and carbon dioxide permits increased efficiency of absorption of the radiation employed. Superatmospheric pressure is, therefore preferred in gas phase reactions also. Am-

bient atmospheric or even lower pressure may, however, be used, in either liquid or gas phase operations.

It is preferred particularly when operating with a mixture of gaseous carbon dioxide and a liquid that circulation or some other form of agitation of the reactants be employed. Agitation insures intimate contact of the reactants during irradiation.

The ratio of CO_2 to the other reactant is not particularly critical and may range from molar ratios of 1:50 to 50:1. It is preferred, however, that the ratio be nearly stoichiometric. Thus the preferred CO_2:other reactant mole ratio is about 1:1.

The temperature utilized in the process may be varied within wide limits from low temperatures in the range of —100° C. and below up to the decomposition temperature of the liquid organic compound or the carboxylic acid product, whichever is lower.

It has been noted that the intensity of the ionizing radiation as it reaches the CO_2:reactant mixture should be at least 50 e.v. The dosage or quantity of radiation employed as accelerated electrons, beta-particles, X-rays or gamma rays must be at least 10^4 rads to produce useful amounts of carboxylation. One rad is the quantity of radiation which will result in an energy absorption of 100 ergs per gram of irradiated material.

The carboxylic acid produced by this invention may be isolated directly by distillation, fractional crystallization, chromatography, selective extraction with a suitable organic solvent or the like. Alternatively, the acid may be first converted to a derivative such as a salt, ester, hydrochloride (of amino acids) or the like, and isolated in the form of the derivative by any of the usual techniques known in the art.

There follow some examples designed to illustrate, but not to limit, representative embodiments of the invention. In them parts are by weight and all pressures are ambient atmospheric unless otherwise specified. Subatmospheric pressures are given in mm. of mercury.

Example I

This example shows the production of cyclohexanecarboxylic acid from cyclohexane and carbon dioxide by means of electron radiation.

Cyclohexane (150 ml.) intimately mixed with a fractional molar quantity of gaseous carbon dioxide was continuously circulated through a glass tube of 15 mm. outside diameter and 13 mm. inside diameter. For 20 cm. of its length the tube was exposed to a beam of 2-m.e.v. (million electron volts) electrons having a current of 5 microamperes per square centimeter of cross section. The temperature of the mixture was 7–8° C. After 6 minutes of irradiation the mixture was distilled at a pressure of 20 mm. from a bath at 50° C. to remove unchanged cyclohexane. The residue in the distillation flask, 0.64 g. of oil, was chromatographed on silicic acid by the procedure of Marvel and Rands, J. Am. Chem. Soc., 72, 2642 (1950). By this means 45 mg. of cyclohexanecarboxylic acid was isolated. For purposes of identification it was converted to p-bromophenacyl cyclohexanecarboxylate, M.P. 89–91° C. The infrared absorption spectrum and X-ray diffraction pattern of the derivative were identical with those of an authentic sample of p-bromophenacyl cyclohexanecarboxylate.

Example II

This example shows the production of phenylacetic acid from toluene.

The procedure of Example I was substantially followed with toluene in place of cyclohexane. The reaction mixture was exposed to the electron beam for 10 minutes. Partition chromatography as described above gave 26 mg. of phenylacetic acid, identified as its p-bromophenyl ester, M.P. 86–88° C. The infrared spectrum of the derivative was identical with that of an authentic specimen.

Example III

This example shows the production of acetic acid from methane.

An equimolar mixture of methane and carbon dioxide was placed in an aluminum box 38" high having a total volume of 125 liters. The top of the box had a section of aluminum foil 0.005" thick and 17" x 1.5" in area. A 500-watt beam of 2-m.e.v. electrons was passed through the aluminum foil into the box for one hour while an equimolar mixture of carbon dioxide and methane was passed through the box at the rate of 2.8 liters/min. The off-gas was bubbled through 100 ml. of water in order to wash volatile acids out of the gas stream. After the irradiation was stopped, the apparatus was flushed out with 300 l. of carbon dioxide. The water through which the off-gas had passed was extracted with five 75-ml. portions of ether. Ten milliliters of chloroform was added and the solution concentrated to a volume of 5 ml. in a spinning band column 24" in height. By partition chromatography, as described in Example I, 15 mg. of acetic acid was isolated. The acid was converted to p-bromophenacyl acetate of M.P. 85–86° C. and with an infrared absorption spectrum identical with that of an authentic sample.

Example IV

This example shows the production of lactic acid from ethanol and solid carbon dioxide by means of electrons.

An intimate mixture of 750 parts of powdered solid carbon dioxide and 242 parts of ethanol in a shallow pan covered with aluminum foil was exposed to 2-m.e.v. electrons. The energy absorbed corresponded to about 1400 watt-sec./g. of ethanol. The solid carbon dioxide was allowed to evaporate and the ethanol solution was concentrated to 1.7 parts of an oil by distillation at a pressure of 15 mm. from a bath at 40° C. By means of partition chromatography as in Example I, 0.17 part of lactic acid was isolated. It was converted to p-bromophenacyl lactate, M.P. 111–112.5° C.; both the infrared absorption spectrum and the X-ray diffraction pattern of the derivative were identical with those of an authentic specimen.

Example V

This example shows the production of heptanecarboxylic acids from heptane.

A mixture of heptane and carbon dioxide was irradiated with 2-m.e.v. electrons for 10 minutes under the conditions of Example I. The reaction mixture was concentrated to 0.95 g. of a yellow oil by distillation at a pressure of 20 mm. from a bath at 50° C. Partition chromatography of the residue under the conditions of Example I gave 55 mg. of a mixture of heptanecarboxylic acids.

Example VI

This example shows the production of cyclohexenecarboxylic acids from cyclohexene.

An intimate mixture of 5000 parts of cyclohexene and 10,000 parts of powdered Dry Ice in a shallow pan covered with aluminum foil was exposed to 1300 watt-sec. of 2-m.e.v. electrons per gram of cyclohexene. The reaction mixture was worked up as in Example IV. Chromatography gave 9.6 parts of a mixture of isomeric cyclohexenecarboxylic acids. Half the mixture of isomers was treated with p-bromophenacyl bromide, giving a mixture of two or three of the three possible isomeric p-bromophenacyl cyclohexenecarboxylates, M.P. 78–83° C. The rest of the mixture was hydrogenated to cyclohexanecarboxylic acid over a platinum oxide catalyst in slightly acidified ethanol. The cyclohexanecarboxylic acid was identified as its p-bromophenacyl ester.

Example VII

This example shows the production of cyclohexane-

carboxylic acid from cyclohexane and carbon dioxide by means of X-radiation.

A mixture of 35 g. of cyclohexane and 37 g. of carbon dioxide at a pressure of 900 lb./in.^{2} in a 100 ml. stainless steel pressure vessel at 25° C. was agitated in a beam of X-rays for 6.5 hours. The X-rays were created by impinging 2-m.e.v. electrons at a current of 250 microamperes on a gold target. The absorption of X-rays in the cyclohexane-carbon dioxide mixture was at a rate of 12,000 rads/min. Chromatography of the reaction mixture as in Example I resulted in the isolation of 5.0 mg. of cyclohexanecarboxylic acid, identified as its p-bromophenacyl ester.

Example VIII

This example shows the production of lactic acid from ethanol and gaseous carbon dioxide by means of X-rays.

A mixture of 39 g. of ethanol and 35 g. of carbon dioxide in a 100-ml. stainless steel pressure vessel was irradiated with X-rays for 8 hours as in Example VII. Lactic acid (2.9 mg.) was isolated by chromatography and identified as its p-bromophenacyl ester.

Example IX

This example shows the preparation of α-alanine from ethylamine by means of electron radiation.

An intimate mixture of 800 parts of powdered solid carbon dioxide and 200 parts of ethylamine, in a shallow pan covered loosely with aluminum foil, was exposed to 2-m.e.v. electrons. The energy absorbed corresponded to about 3300 watt-sec./g. of ethylamine. The solid carbon dioxide was allowed to evaporate and the remaining solution concentrated to 2.5 parts of viscous oil by distillation at a pressure of 25 mm. from a bath at 90° C. By means of paper chromatography it was shown that α-alanine was a principal component of this oil.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. The process which comprises irradiating an intimate mixture of carbon dioxide and an organic compound possessing a carbon atom bonded to hydrogen and to three other atoms with at least 10^4 rads of electrons having an energy of at least 50 electron volts and subsequently separating at least one carboxylic acid from the irradiated mixture.

2. The process of claim 1 in which the organic compound is a member of the group consisting of aliphatic, cycloaliphatic and arylaliphatic hydrocarbons, alcohols and amines possessing at least one carbon atom bonded to a hydrogen atom and to three other atoms.

3. The process which comprises irradiating a mixture of carbon dioxide and cyclohexane with at least 10^4 rads of electrons having an energy of at least 50 electron volts and subsequently separating at least one carboxylic acid from the irradiated mixture.

4. The process which comprises irradiating a mixture of carbon dioxide and toluene with at least 10^4 rads of electrons having an energy of at least 50 electron volts and subsequently separating at least one carboxylic acid from the irradiated mixture.

5. The process which comprises irradiating a mixture of carbon dioxide and ethanol with at least 10^4 rads of electrons having an energy of at least 50 electron volts and subsequently separating at least one carboxylic acid from the irradiated mixture.

6. The process which comprises irradiating a mixture of carbon dioxide and heptane with at least 10^4 rads of electrons having an energy of at least 50 electron volts and subsequently separating at least one carboxylic acid from the irradiated mixture.

7. The process which comprises irradiating a mixture of carbon dioxide and cyclohexene with at least 10^4 rads of electrons having an energy of at least 50 electron volts and subsequently separating at least one carboxylic acid from the irradiated mixture.

8. The process which comprises irradiating an intimate mixture of carbon dioxide and an organic compound possessing a carbon atom bonded to hydrogen and to three other atoms with at least 10^4 rads of X-rays having an energy of at least 50 electron volts and subsequently separating at least one carboxylic acid from the irradiated mixture.

9. The process of claim 8 in which the organic compound is a member of the group consisting of aliphatic, cycloaliphatic and arylaliphatic hydrocarbons, alcohols and amines possessing at least one carbon atom bonded to a hydrogen atom and to three other atoms.

10. The process which comprises irradiating a mixture of carbon dioxide and cyclohexane with at least 10^4 rads of X-rays having an energy of at least 50 electron volts and subsequently separating at least one carboxylic acid from the irradiated mixture.

11. The process which comprises irradiating a mixture of carbon dioxide and toluene with at least 10^4 rads of X-rays having an energy of at least 50 electron volts and subsequently separating at least one carboxylic acid from the irradiated mixture.

12. The process which comprises irradiating a mixture of carbon dioxide and ethanol with at least 10^4 rads of X-rays having an energy of at least 50 electron volts and subsequently separating at least one carboxylic acid from the irradiated mixture.

13. The process which comprises irradiating a mixture of carbon dioxide and heptane with at least 10^4 rads of X-rays having an energy of at least 50 electron volts and subsequently separating at least one carboxylic acid from the irradiated mixture.

14. The process which comprises irradiating a mixture of carbon dioxide and cyclohexene with at least 10^4 rads of X-rays having an energy of at least 50 electron volts and subsequently separating at least one carboxylic acid from the irradiated mixture.

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