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This invention is a method of preparing 1-aryl-1,2-alkylene carbonates. The method involves cathodic reduction of substituted aromatic hydrocarbons having certain characteristics in the presence of carbon dioxide. In a preferred embodiment the starting material is styrene in which case the product obtained is 1-phenyl-1,2-ethylene carbonate, otherwise known as styrene carbonate. Thus,

Equation 1
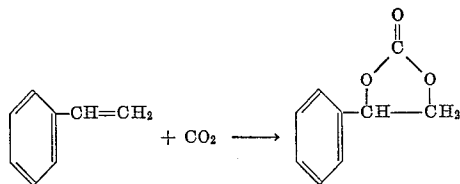
According to the invention 1-aryl-1,2-alkylene carbonates are obtained from hydrocarbons of the type specified hereinafter by electrolyzing the hydrocarbon, at the cathode of an electrolytic cell, at a potential greater than its half-wave potential, i.e., by cathodic reduction, in the presence of (1) an electrolyte, (2) a solvent, and (3) carbon dioxide. The half-wave potential is a property which is determined polarographically according to the procedure described in, for example, Kirk and Othmer, Encyclopedia of Chemical Technology, vol. 10, pp. 886–890 (1947). It is the potential of the inflection point of a current potential diagram obtained under the described conditions. It is a measure of the potential at which electrolytic reaction, usually reduction, takes place in the material in question. The electrolytic reaction which occurs at the cathode is one of reduction, i.e., the addition of one or two electrons, and the potential required to effect same is generally negative. The electrolytic reaction which occurs at the anode is one of oxidation, i.e., the loss of one or two electrons, and the potential required to effect same is generally positive. All half-wave potentials herein are cathodic half-wave potentials and are, in addition, all expressed as potentials relative to a calomel reference electrode.

As described, the electroyltic reaction which occurs in the method of the invention is reduction, i.e., the addition of electrons to the hydrocarbon starting material. More specifically, it is the addition of two electrons. With some hydrocarbons such as styrene and almost all other hydrocarbons suitable as starting materials for the present purpose the addition of two electrons thereto occurs at a single potential. In such a case the current-potential diagram referred to above has only a single inflection point and would be referred to by those skilled in the art as having a single wave. Other hydrocarbons such as naphthalene add two electrons in two steps. The first electron adds at a certain potential and the second electron adds at a different and larger potential. For example, the first electron might add at −1.2 volts and the second electron might add at −2.0 volts. In this case the current-potential diagram has two inflection points and would be referred to by those skilled in the art as having two waves. Although it would be technically correct to refer to such a hydrocarbon as having two half-wave potentials, since reduction occurs at each of two

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different potentials, for the present purpose the term half-wave potential as applied to such a compound means the second or larger half-wave potential, i.e., it means the potential of the second wave or the half-wave potential representing the addition of the second electron. In the above example the half-wave potential for the present purpose is −2.0 volts and not −1.2 volts.

The suitable starting materials for the present purpose are completely defined by the following characteristics which they all possess. One, they are hydrocarbons. In addition, they contain one, and only one, aryl nucleus. An aryl ring is the carbocyclic ring characteristic of benzene. An aryl nucleus is an aryl ring, either alone as in benzene or condensed with other rings either aryl or otherwise as in naphthalene, Tetralin, anthracene, phenanthrene, indan, etc. Preferably the nucleus contains one or two rings and in the latter case they are preferably both six-membered rings. Furthermore, all rings in the aryl nucleus are preferably aryl rings. As indicated the starting materials contain exactly one aryl nucleus. Although anthracene contains 3 rings it has only 1 aryl nucleus because the rings are all condensed to form a single condensed ring system. Biphenyl has two rings and since they are not condensed they represent two aryl nuclei. Binaphthyl has 4 rings and even though each ring is condensed there are two nuclei because the rings are condensed to form two rather than one condensed ring systems.

Another characteristic of starting materials suitable for the present purpose is the manner in which the valences of the carbon atoms in the aryl nucleus are satisfied. Some valences will, of course, be satisfied by other nuclear carbon atoms. Those not so satisfied can be satisfied by either hydrogen, saturated aliphatic radicals or monoolefinic aliphatic radicals. In addition, there will be at least one monoolefinic aliphatic radical attached to a nuclear carbon atom of an aryl ring in which monoolefinic radical the double bond is conjugated with one of the double bonds in the aryl ring. Such a monoolefinic aliphatic radical is present in styrene, vinylnaphthalene, 7-vinyltetralin, 1-phenyl-butene-1, vinyltoluene, butylvinylnaphthalene, and the like but is not present in 2-vinyltetralin, 1-phenylpropene-2, 1-naphthylbutene-3. Preferably no saturated aliphatic groups are attached to the aryl nucleus but if any are present they preferably contain 1–4 carbon atoms. Similarly there is preferably only one monoolefinic aliphatic group attached to the aryl nucleus and it preferably contains 2–4, more preferably 2, carbon atoms, but any others present also preferably contain 2–4 carbon atoms. Styrene is the preferred starting material.

As described the products obtained by the method of the invention are 1-aryl-1,2-alkylene carbonates. The carbonate radical in the product is attached to the two carbon atoms in the monoolefinic radical in the starting material which contained unsaturation conjugated with unsaturation in an aryl ring. This is more clearly apparent from an examination of Equation 1 supra. The product also contains an aryl substituent in the 1-position, the aryl substituent being the aryl nucleus (and any substituents thereon) to which the monoolefinic group containing conjugated unsaturation was attached.

The cathodic reduction of the invention is carried out in the presence of an electrolyte, this being necessary since the hydrocarbon starting materials are not themselves conductive. In addition, it is desirable, but not essential, that the electrolyte have a higher half-wave potential than the potential employed in the electrolysis, which in turn will be higher than the half-wave potential of the hydrocarbon starting material, in order to avoid reduction of the electrolyte simultaneously with the de-

sired reduction of the hydrocarbon. This is not essential since reduction of the electrolyte does not prevent reduction of the hydrocarbon also but reduction of the electrolyte represents needless power consumption and often results in the formation of undesirable by-products. The hydrocarbon starting materials of the invention have rather high reduction potentials, i.e., the half-wave potential is a rather large negative voltage. The electrolyte preferably has a higher reduction potential; its half-wave potential should be a larger negative voltage, i.e., more negative, than that of the hydrocarbon. For example, a preferred electrolyte for use when styrene which has a half-wave potential of −2.5 volts is being electrolyzed at a potential of −2.6 volts would be tetraethylammonium bromide which has a half-wave potential of greater than −2.7 volts. If the electrolysis was being conducted at a potential of −2.9 volts tetrabutylammonium bromide would be a preferred electrolyte because its half-wave potential is greater than −3 volts.

Selection of the electrolyte so as to avoid reduction of same in practicing the invention requires knowledge of the half-wave potential of various electrolytes. Similarly, selection of the potential employed requires, as more fully discussed hereinafter, knowledge of the half-wave potential of the hydrocarbon starting material. The half-wave potential is a property readily determinable by known procedures. In addition, considerable information concerning half-wave potentials of various hydrocarbons and electrolytes is contained in K. Schwabe, Polarographie and Chemische Konstitution Organischer Verbindungen, (1947). Since the tetraalkylammonium halide have half-wave potentials generally higher than the hydrocarbon starting materials of the invention they are the preferred electrolytes.

The cathodic reduction according to the invention is also carried out in the presence of a mutual solvent for both the hydrocarbon and the electrolyte, the use of the solvent being necessary since the electrolyte used is generally insoluble in the hydrocarbon starting material used. As in the case of the electrolyte it is desired, but not essential, that the solvent have a decomposition potential more negative than the potential employed in the electrolysis in order to avoid reduction of the solvent simultaneously with reduction of the hydrocarbon. Decomposition potential is defined in the aforesaid Kirk and Othmer reference and constitutes the potential at which the current begins to turn sharply upward. In the case of a solvent, the decomposition potential is more meaningful than is the half-wave potential since the solvent frequently does not exhibit the typical S-shaped curve that admits of the determination of a half-wave potential. As with half-wave potential, the decomposition potential is negative for cathodic decomposition and positive for anodic decomposition. All decomposition potentials referred to herein are for cathodic decomposition.

Similarly to half-wave potential, decomposition potential is a property which is readily determinable by known procedures and the criteria for selection of a preferred solvent are therefore available to a person skilled in the art. The preferred solvents for the present purpose are dioxane, aqueous dioxane, dimethylacetamide, acetonitrile, and dimethylformamide since these solvents have decomposition potentials higher, i.e., more negative, than −3 volts which is substantially higher than the potentials which will be employed in most cases. More preferably the solvent is dimethylformamide.

As described previously the electrolysis is also carried out in the presence of CO_2. The CO_2 can be added to the electrolysis medium, i.e., to the solution of the hydrocarbon and electrolyte in the solvent, in any manner desired, but it is generally most convenient to merely bubble gaseous CO_2 into the electrolysis medium. The amount of CO_2 consumed will vary but will depend primarily upon the rate at which the hydrocarbon starting material is reduced.

The potential employed should be greater than the half-wave potential of the hydrocarbon starting material. This requirement is, of course, inherent in the term cathodic reduction. Also as described hereinbefore, the potential employed is preferably less negative than both the decomposition potential of the solvent and the half-wave potential of the electrolyte. Preferably the potential is about 0.1–0.6 volt higher than the half-wave potential of the hydrocarbon.

During the electrolysis the hydrocarbon must be present at the surface of the cathode. This requirement is, of course, also inherent in the term cathodic reduction. Preferably the electrodes are separated by a diaphragm which is permeable to the solvent and electrolyte but impermeable to the hydrocarbon starting material in order to prevent migration of the starting material to the anode and oxidation at that electrode. Conventional diaphragm materials such as porous Alundum can be used for this purpose.

The temperature and pressure at which the electrolysis is carried out can vary considerably but do in some cases have some influence upon the yield of the alkylene carbonate product. Preferably the temperature is in the range of −30° C. to 50° C. although higher temperatures of, say, 100° C. or lower temperatures of say −50° C. can be employed if desired. The temperature at which the electrolysis is carried out will in conjunction with the CO_2 partial pressure influence the amount of CO_2 dissolved in the electrolysis medium and this in turn may, in conjunction with the amount of hydrocarbon starting material in the electrolysis medium, have some influence on the rate at which the alkylene carbonate is formed or the yield thereof. As the temperature increases the solubility of CO_2 in the electrolysis medium decreases and thus the reaction rate tends to decrease. As the temperature decreases the solubility of CO_2 in the electrolysis medium increases and this tends to increase the amount of by-products formed at the expense of the desired alkylene carbonate product. In most cases the electrolysis medium, or the catholyte in the case where a diaphram is used, will be 40–100% saturated with respect to the hydrocarbon starting material but can if desired be more saturated, e.g., saturated. In any event, in the temperature range of −50° C. to 50° C. optimum results are obtained with a CO_2 partial pressure of about 0.01–15 p.s.i.a., preferably 0.1–10 p.s.i.a. although satisfactory results are also obtained in this temperature range with CO_2 partial pressures of up to about 15–30 p.s.i.a. The preferred practice is to bubble CO_2 into the electrolysis medium in a cell open to the atmosphere so that any CO_2 which does not dissolve in the electrolysis medium passes out of the cell. At temperatures above about 50° C. the CO_2 pressure is preferably about 15–30 p.s.i.a. although higher CO_2 pressures up to about 100 p.s.i.a. or even lower pressures can often be used successfully. Another manner of describing the preferred temperature and pressure conditions is in terms of the concentration of CO_2 in the electrolysis medium. Preferably this CO_2 concentration is maintained at less than 2 moles of CO_2 per mole of reduced hydrocarbon in the electrolysis medium.

A variety of materials can be used as the electrodes. Examples of suitable materials are zinc, lead, tin, mercury, cadmium, etc., as the cathode and platinum, palladium, gold, etc. as the anode. Mercury is the preferred cathode material.

The 1-aryl-1,2-alkylene carbonate product can be separated from the electrolyte, solvent, any unreacted hydrocarbon and any by-products in any convenient manner. Frequently the solvent and electrolyte can be separated by a vacuum distillation. Any by-products can be separated from the resulting residue by extraction with dilute alkali leaving a mixture of the alkylene carbonate product and any unreacted hydrocarbon. The alkylene carbonate product can be separated from this mixture by fractional

crystallization. Another suitable procedure for separating the alkylene carbonate product from the solvent, electrolyte, unreacted hydrocarbon, and any by-products, is elution chromatography, this technique being specifically illustrated in the subsequent example. Other procedures will be readily apparent to those skilled in the art.

The following example illustrates the invention more specifically:

Example

The electrolysis cell contains a pool of mercury on the bottom as the cathode and a platinum anode. A porous Alundum diaphram separates the cell into an anode chamber and a cathode chamber. The anolyte is a 0.15 molar solution of tetrabutylammonium bromide in dimethylformamide. The half-wave potential of tetrabutylammonium bromide is greater than —3 volts. The catholyte is a similar solution containing 5% styrene by weight of the electrolyte-solvent mixture in the catholyte. The cell contains means for bubbling CO_2 into the catholyte as well as means for controlling the temperature of both the anolyte and catholyte. The surface of the catholyte (and the anolyte) is exposed to the atmosphere so that any CO_2 which is bubbled into the electrolysis medium but does not dissolve therein escapes from the surface of the catholyte.

The above described styrene solution is maintained at 25° C. while being electrolyzed at a potential of —3.0 volts for a period of 30 hours. CO_2 is bubbled into the catholyte continuously during the electrolysis, the amount of CO_2 being adjusted so that CO_2 is continuously escaping from the surface of the catholyte.

At the end of the electrolysis a 100 ml. sample of the catholyte is withdrawn and washed twice with 25% aqueous HCl. The washed catholyte is then extracted with 100 mls. ether. The ether extract is discarded and the washed, ether extracted catholyte is then extracted with 100 mls. benzene. The benzene extract is dried, filtered, and then evaporated to dryness on a steam bath. 1-phenyl-1,2-ethylene carbonate is isolated from the residue on a chromatographic column containing as adsorbent, 6% silicone rubber on alumina. Identification of the carbonate product is made by comparing its infra-red and

mass spectra and its melting point with the same properties of a known sample of 1-phenyl-1,2-ethylene carbonate. The yield of 1-phenyl-1,2-ethylene carbonate is 7.1% based on styrene.

Substantially analogous results are obtained with other starting materials of the type specified herein and with other electrolytes and solvents.

The invention claimed is:

1. Method which comprises electrolyzing a substituted aromatic hydrocarbon characterized in that it contains exactly one aryl nucleus, the nuclear carbon atoms of said nucleus having attached thereto only other nuclear carbon atoms, hydrogen, saturated aliphatic radicals, and monoolefinic aliphatic radicals, there being present at least one monoolefinic aliphatic radical in which the double bond is conjugated with unsaturation in an aryl ring of said nucleus, said electrolyzing being (1) in an electrolytic cell containing an anode and cathode, (2) at a potential more negative than the half-wave potential of said hydrocarbon, (3) in the presence of an electrolyte, (4) in the presence of a mutual solvent for said electrolyte and said hydrocarbon, and (5) in the presence of CO_2, said hydrocarbon being present at the surface of said cathode during said electrolysis, whereby there is formed a 1-aryl-1,2-alkylene carbonate, and separating said carbonate from said electrolyte and solvent.

2. Method according to claim 1 wherein said hydrocarbon is styrene.

3. Method according to claim 2 wherein said solvent is dimethylformamide.

4. Method according to claim 3 wherein said hydrocarbon is styrene.

5. Method of according to claim 1 wherein said electrolyzing is carried out at a temperature in the range of —30° C. to 50° C. and wherein the partial pressure of said CO_2 is 0.01–15 p.s.i.a.

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