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(21) Application No. 35784/77 (22) Filed 25 Aug. 1977 (19)
 (31) Convention Application No. 27825 (32) Filed 30 Sept. 1976 in
 (33) Italy (IT)
 (44) Complete Specification published 3 Sept. 1980
 (51) INT. CL.³ C07C 69/96
 (52) Index at acceptance

C2C 20Y 30Y 358 43X 550 FB YT

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(54) PRODUCTION OF ESTERS OF CARBONIC ACID

(71) We, ANIC S.p.A., Via M. Stabile 216, Palermo, Italy, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by 5 which it is to be performed, to be particularly described in and by the following statement:—

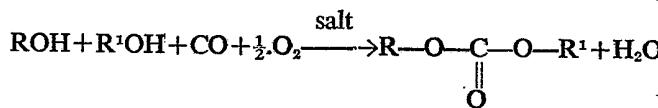
This invention relates to a process for producing esters of carbonic acid.

10 Esters of carbonic acid are known, and they find a use as solvents and as polymerizing agents in transesterification reactions and glycols and bisphenols in the production of polycarbonates.

15 The present invention provides a process for producing an ester of carbonic acid, which comprises reacting an alcohol with carbon monoxide in the presence of a salt

of a metal belonging to Group IB, IIB or 20 VIII of the Periodic Table (hereinafter referred to), oxygen being present during at least part of the process to enable the metal salt to undergo oxidation, the metal salt being introduced to the reaction in uncomplexed form, and the reaction being effected 25 in the absence of complexing agents other than the CO present as a reactant, wherein in the salt the metal ion is initially in its lowest possible positive oxidation state and is bound to the lowest possible number of inorganic anions. The use of monovalent copper salts has proved to be particularly 30 advantageous.

The reaction pattern can, for convenience, 35 be summarized as follows:—



wherein each of R and R¹, which are the 45 same or different, is preferably a hydrocarbon radical, more preferably an alkyl, aryl or cycloalkyl radical. The salt acts as a catalyst in the reaction; without wishing to be bound by this explanation, it appears that the salt with the metal in a relatively oxidized state reacts with the alcohol(s) and carbon monoxide to produce the ester, 50 whereby the metal of the salt is reduced to a relatively reduced state; the metal of the salt in a relatively reduced state is oxidized by the oxygen at some stage of the process.

55 The reaction is conveniently carried out by dispersing or dissolving the salt of the metal in a solvent which can be alcohol itself or an inert diluent.

60 The advantage, mentioned above, stemming from the use of a salt having a restricted number of inorganic anions is considerable, because there is no, or no significant, formation of a high acidity during progress of the reaction. The reaction system remains at pH values of a weakly acidic

65 character during the entire reaction run, so that the reaction is not impaired and proceeds to a good carbonate ester yield without experiencing the formation of any appreciable quantities of by-products.

70 As outlined above, the reaction can be carried out either by dispersing or dissolving the metal salt in a dispersion or solvent medium: through the resulting dispersion or solution a stream of CO and O₂ is delivered, the carbon monoxide and oxygen being fed either separately or admixed together, either continuously or in alternating cycles.

75 The desired product can be separated 80 from the reaction mixture by means of simple physical procedures. In the case of dispersions, for example, filtration is sufficient to remove the catalyst, thus separating the solution which contains the carbonate which can then be recovered by rectification or crystallization.

85 The method of the invention can be carried out within a wide range of pressures

and temperatures and the upper limits are a function of, for example, the stability of the compounds which are employed. Generally speaking, the operating temperature is 5 in the range from 70°C to 200°C, and each of the CO and O₂ pressures is greater than atmospheric pressure.

The Periodic Table referred to herein is that on page 149 of "Tables of Physical 10 and Chemical Constants" by G. W. C. Kaye

and T. H. Laby, 14th Edition, in which Group IB consists of Cu, Ag and Au; Group IIB consists of Zn, Cd and Hg; and Group VIII consists of Fe, Co, Ni, Ru, Rh, Pd, Os, Ir and Pt.

In the following Examples, which illustrate the present invention, the terms "conversion", "yield" and "selectivity" are as defined below:

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$$\text{conversion, C (\%)} = \frac{\text{amount of reactant actually converted}}{\text{amount of reactant available for conversion}} \times 100$$

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$$\text{selectivity, S, (\%)} = \frac{\text{amount of desired product actually produced}}{\text{amount of reactant actually converted}} \times 100$$

$$\text{yield, Y, (\%)} = \frac{\text{amount of desired product actually produced}}{\text{amount of reactant available for conversion}} \times 100$$

It can be seen that Y=C×S. Of these 35 Examples, Examples 4 and 8 are comparative as oxygen is absent during the process.

pressure of 10 atmospheres (gauge) for 60 minutes. This oxidized the CuCl to cupric chloride. Subsequently, CO was introduced under 30 atmospheres (gauge) constant pressure and the temperature was raised to 100°C. The reaction lasted as long as 90 minutes. On completion of the reaction the cuprous chloride was found to be completely in reduced form (i.e. with copper in the monovalent state). It appeared that of the catalyst 95% was responsible for producing dimethyl carbonate and 5% for oxidizing CO to CO₂. The dimethyl carbonate yield was 95%. The selectivity methanol towards dimethyl carbonate was total.

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EXAMPLE 1
A 200-ml, Teflon-lined autoclave was 40 charged with 100 ml methanol and 18 grams of CuBr. The word "Teflon" is a registered Trade Mark for a fluorinated hydrocarbon. The system was oxidized with O₂ at 60°C under a pressure of O₂ of 5 atmospheres (gauge) for 90 minutes, the cuprous bromide being oxidized to cupric bromide. Subsequently, CO was introduced until a total pressure of 12 atmospheres (gauge) was attained, and the temperature was raised to 45 80°C. Carbon monoxide was replaced in the system as it was used up in the reaction, so as not to alter the total pressure. The reaction was completed after 30 minutes, and the resulting solution was analyzed by gas 50 chromatographical analysis. There was obtained a complete conversion of the cupric bromide to cuprous bromide; it appeared that 95% of the catalyst used was responsible for the production of dimethyl carbonate, and that the residual (5%) of catalyst was responsible for oxidizing carbon monoxide to carbon dioxide. There have been carried out 4 similar subsequent cycles and only a slight increase in selectivity towards 55 CO₂ with time was observed. In the fourth cycle the molar ratio CO₂:dimethyl carbonate was 1:9.

EXAMPLE 2

The apparatus described in Example 1 70 was charged with 100 ml methanol and 20 grams of CuCl, and the system was oxidized with O₂ at 80°C and under an O₂

EXAMPLE 3

Into the apparatus of Example 1 there were introduced 16.4 grams of CuClO₄ and 26 grams of methanol. The system was oxidized with O₂ at 100°C and under a pressure of 5 atmospheres (gauge) for 20 minutes, and then reduced with CO under 50 atmospheres (gauge) at 100°C for 2 hours. On completion of the reaction the copper was in a totally reduced form (i.e. CuCl). The dimethyl carbonate yield was over 95%. Of the catalyst, 95% was responsible for producing the dimethylcarbonate, and 5% for oxidizing CO to CO₂ and the selectivity of methanol towards dimethyl carbonate was total.

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EXAMPLE 4 (Comparative)

The apparatus of Example 1 was charged with 15 grams of methanol and 10 grams of CuCl₂. To this system there were added 3.9 grams of sodium methylate in 20 grams 110 methanol, to such an extent as to neutralize

one of the two chloride ions bound to the copper. The reaction mixture was brought to 100°C and placed under a pressure of 60 atmospheres (gauge) of CO. After two hours a complete reduction of CuCl₂ to CuCl was experienced, and dimethyl carbonate was obtained with a yield of 90% approx of the theoretical. There was noted the formation of small amounts of methyl chloride and dimethyl ether, but less than 0.02%.

EXAMPLE 5

A 6 litre, ceramic-lined autoclave was charged with 3 litres of methanol and 480 grams of CuCl, the temperature was raised to 70°C and O₂ was introduced under a pressure of 8 atmospheres (gauge) until a complete oxidation of the cuprous chloride to cupric chloride was achieved, which was completed within an hour approximately. Subsequently, the excess of O₂ was vented, and CO introduced under a pressure of 15 atmospheres (gauge) the pressure being kept constant. Within 3 hours the reduction of cupric chloride to cuprous chloride was total. The selectivity of the catalyst towards dimethyl carbonate was over 95%, and the remaining copper catalyst oxidized CO to CO₂. The selectivity of methanol towards dimethyl carbonate was total. In the three subsequent cycles the trend of the reaction was substantially the same as before. Only a slight increase of CO₂ between one reaction cycle and the next was observed.

EXAMPLE 6

The apparatus described in Example 5 was charged with 3 litres of methanol and 480 grams of CuCl, the temperature raised to 100°C and O₂ was fed in under a pressure of 10 atmospheres (gauge) until a complete oxidation of cuprous chloride to cupric chloride was achieved, which took about 30 minutes. The excess oxygen was vented and CO was fed in under a pressure of 20 atmospheres (gauge), the temperature being maintained at 120°C. After 20 minutes, the reaction was completed and the selectivity of catalyst towards dimethyl carbonate was 92%. The remainder of the copper catalyst oxidized CO to CO₂.

EXAMPLE 7

The apparatus described in Example 5 was charged with 3 litres of methanol and 480 grams of CuCl. The thermostatically controlled system was fed simultaneously at 102°C with 150 normal litres an hour of CO and 50 normal litres an hour of O₂ under a total pressure of 30 atmospheres (gauge). The system was continually vented by discharging 50 normal litres hourly of a gaseous mixture which was essentially com-

posed of 97% CO, from 2% to 3% CO₂ and from 0.1% to 0.4% O₂; after a 4-hour run the conversion of methanol was 30% and the selectivity of methanol relative to dimethyl carbonate was 95%.

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EXAMPLE 8 (Comparative)

The apparatus described in Example 1 was charged with 16 grams CuSO₄ and 30 ml methanol: to the system there were added 3.8 grams of lithium methoxide in 10 ml methanol so as to neutralize one half of the sulphate ion. CO was fed in under 50 atmospheres (gauge) and the temperature was brought to 100°C. After two hours the copper was entirely reduced to Cu₂SO₄. Dimethyl carbonate was obtained with a yield of 75% relative to the copper compound converted at the end of the reaction: the remaining copper had oxidized CO to CO₂. The selectivity of methanol towards dimethyl carbonate was total.

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WHAT WE CLAIM IS:—

1. A process for producing an ester of carbonic acid, which comprises reacting an alcohol with carbon monoxide in the presence of a salt of a metal belonging to Group IB, IIB or VIII of the Periodic Table (hereinbefore referred to), oxygen being present during at least part of the process to enable the metal salt to undergo oxidation, the metal salt being introduced to the reaction in uncomplexed form, and the reaction being effected in the absence of complexing agents other than the CO present as a reactant, wherein in the salt the metal ion is initially in its lowest possible positive oxidation state and is bound to the lowest possible number of inorganic anions.

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2. A process according to claim 1, wherein the salt is a salt of monovalent copper.

3. A process according to either preceding claim, wherein the reaction is carried out at a temperature in the range from 70°C to 200°C.

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4. A process according to any preceding claim, wherein the reaction is carried out under a pressure greater than atmospheric pressure.

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5. A process according to any preceding claim, wherein the reaction is carried out with the alcohol as the only reaction medium.

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6. A process according to any one of claims 1 to 4, wherein the reaction is carried out in the presence of a diluent which is inert with respect to the reaction.

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7. A process according to claim 1, substantially as described in any one of the foregoing Examples.

8. An ester of carbonic acid, whenever produced by a process according to any preceding claim.

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Printed for Her Majesty's Stationery Office by Burgess & Son (Abingdon), Ltd.—1980.
Published at The Patent Office, 25 Southampton Buildings, London, WC2A 1AY,
from which copies may be obtained.