

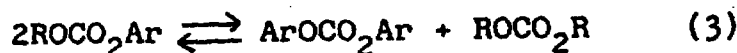
Description

This invention relates to a process for producing an aromatic carbonate compound. More specifically, it relates to an easily purifiable aromatic carbonate compound in a high yield and a high selectivity by reacting a phenolic compound with a di-aliphatic carbonate or an aliphatic-aromatic carbonate in the presence of a specific catalyst.

It is well known to produce an aliphatic-aromatic carbonate, a di-aromatic carbonate or an aromatic carbonate composed of a mixture of both by reacting a phenolic compound with a di-aliphatic carbonate or an aliphatic-aromatic carbonate. This reaction is shown by the following reaction equations.



or



In the reactions (1) and (2), the equilibrium constants K_1 and K_2 shown below are low, the equilibrium is shifted to the starting material side, and the reaction rate is slow. Hence, the yields of ROCO_2Ar and ArOCO_2Ar are very low.

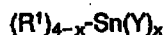
$$K_1 = \frac{\{\text{ROCO}_2\text{Ar}\} \{\text{ROH}\}}{\{\text{ROCO}_2\text{R}\} \{\text{ArOH}\}}$$

$$K_2 = \frac{\{\text{ArOCO}_2\text{Ar}\} \{\text{ROH}\}}{\{\text{ROCO}_2\text{Ar}\} \{\text{ArOH}\}}$$

Accordingly, many attempts have been made to select suitable catalysts for increasing the yield of the product in this reaction system.

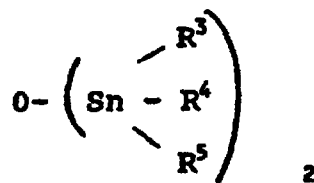
For example, JP-A-105032/1976 discloses Lewis Acids, metal compounds and transition metal compounds capable of forming Lewis acids, and cites SnX_4 (X is halogen, acetoxy, alkoxy or aryloxy) as preferred examples.

JP-A-48733/1979 and EP-A-0000 879 disclose an organotin catalyst represented by the following formula



wherein Y represents the OCOR^2 group, OH group or OR^2 group, R^1 and R^2 are identical or different and each represents an alkyl group having 1 to 12 carbon atoms, an aryl group having 6 to 12 carbon atoms, or an alkylaryl group having 7 to 12 carbon atoms, and X is an integer of 1 to 3, which has no tin-halogen bond.

JP-A-48733/1979 and EP-A-879 also disclose a catalyst of formula



10 wherein R^3 and R^4 are the same or different and are defined as for R^2 , and R^5 is defined as for R^2 or is $-OR^6$ in which R^6 is defined in the same way as R^2 .

JP-A-63023/1979 discloses a tin alkoxide represented by the following formula

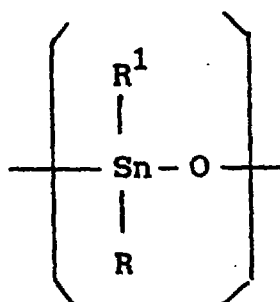


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wherein R and R^1 represent a hydrocarbon group and l is an integer of 0 to 2.

JP-A-169444/1985 discloses a polymeric tin compound represented by the following formula

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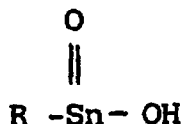
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wherein R and R^1 represent a hydrocarbon group.

JP-A-169445/1985 discloses a tin compound of the following formula

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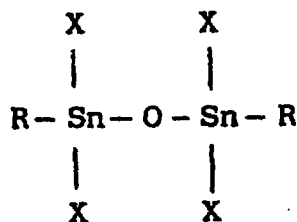


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wherein R represents a hydrocarbon group or a hydrocarbon-oxy group.

JP-A-277345/1987 states that a tin compound represented by the following formula

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wherein R represents an alkyl group having 1 to 12 carbon atoms or an aryl group, and X is halogen, alkoxy, carboxylate or phenolate.

55 can be used as a reaction catalyst for the production of aromatic carbonates.

These previously known tin-containing catalysts increase the yields of the products in the reaction systems to some extent, but still have insufficient catalytic activity. Accordingly, this makes it difficult to purify the products.

JP-A-105032/1976 cited above also describes AlX_3 , TiX_3 , TiX_4 , UX_4 , VOX_3 , VX_5 , ZnX_2 , and FeX_3 - (where X is halogen, acetoxy, alkoxy or aryloxy) as preferred examples of the Lewis acids and metal compounds and transition metal compounds capable of forming Lewis acids. However, the Lewis acids are corrosive and are not desirable for the reaction apparatus and the like. The method involving the use of the above compounds is low in the yield of the desired product, and cannot be said to be commercially advantageous.

The present invention provides a process for producing an aromatic carbonate compound selected from aliphatic-aromatic carbonates, di-aromatic carbonates and mixtures of these, which comprises reacting a phenolic compound represented by formula (I)



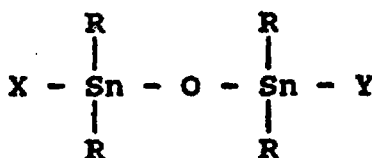
where Ar represents an aromatic compound residue of a substituted or unsubstituted benzene, naphthalene, anthracene or tetralin ring with a di-aliphatic carbonate compound represented by formula (II)



where R' represents a monovalent aliphatic hydrocarbon group having 1 to 12 carbon atoms and the two R' may link each other to form an alicyclic ring or an aliphatic-aromatic carbonate represented by formula (III)



wherein Ar is as defined in formula (I) and R' is a monovalent aliphatic hydrocarbon group have 1 to 12 carbon atoms in the presence of a catalyst selected from Sc_2O_3 , ScCl_2 , $\text{Sc}(\text{OH})_3$, ScCl_3 , ScF_3 ; $\text{Mo}(\text{CH}_3\text{COCHCOCH}_3)_3$, $\text{Mo}(\text{CO})_6$, Mo_2O_3 , $\text{Mo}(\text{OH})_3$, MoO_2 , $\text{C}_5\text{H}_5\text{MoC}_6\text{H}_5$; $\text{Mn}_2(\text{CO})_{10}$, $\text{Mn}(\text{CH}_3\text{COCHCOCH}_3)_3$, MnO_2 , KMnO_4 , Mn_2O_7 , MnCl_2 ; $\text{NaAuCl}_2 \cdot 2\text{H}_2\text{O}$, AuCl_3 , AuF_3 ; $\text{Bi}(\text{OCOCH}_3)_3$, BiH_3 , Mg_5Bi_2 ; $\text{La}(\text{OCOCH}_3)_2$, $\text{La}(\text{OH})_3$, $\text{Ce}(\text{OH})_3$, $\text{Pr}(\text{OH})_3$, $\text{Nd}(\text{OH})_3$, $\text{Pm}(\text{OH})_3$, $\text{Sm}(\text{OH})_3$, $\text{Eu}(\text{OH})_3$, $\text{Gd}(\text{OH})_3$, $\text{Lu}(\text{OH})_3$, $\text{LuCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{La}(\text{NO}_3)_3$, La_2O_3 ; $\text{Cr}(\text{CH}_3\text{COCHCOCH}_3)_3$, $\text{Cr}(\text{CO})_6$, Cr_2O_3 , $\text{Cr}(\text{OH})_3$, $\text{K}_2\text{Cr}_2\text{O}_7$, $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$, $\text{Cr}(\text{H}_2\text{O})_6\text{Cl}_3$, CrO_3 ; $\text{W}(\text{CO})_6$, WO_2 , WO_3 , WF_6 , WCl_6 , WBr_6 ; $\text{Ga}(\text{NO}_3)_3$, GaCl_2 , GaCl_3 ; In_2O_3 , $(\text{InH}_3)_n$, InCl_2 ; TeCl_4 , TeH_2 , TeF_6 , TeO_2 , TeCl_4 , H_2TeCl_6 , TeO , SnO and/or a tin compound represented by the following formula



wherein X and Y are identical or different and each represents OH, SCN, OR' , OCOR' or a halogen atom, R' represents an alkyl or aryl group, X and Y are not alkoxy groups at the same time, and R represents an alkyl or aryl group, with the proviso that X and Y are not simultaneously OR' .

The present invention further provides a process for producing a di-aromatic carbonate, which comprises heating the aliphatic-aromatic carbonate of formula III or a mixture of it with a di-aromatic

carbonate obtained by the process as defined above in the presence of a catalyst as defined above.

The present invention is based on the new finding that in the reaction of a phenolic compound with a dialiphatic carbonate or an aliphatic-aromatic carbonate, the use of a catalyst as defined above can give an easily purifiable aromatic carbonate in a high yield and a high selectivity as compared with the use of known reaction catalysts.

In the process of the invention, the above catalysts may be used either singly or in combination with each other.

By using the catalysts defined above, the reaction of a phenolic compound with a dialiphatic carbonate or an aliphatic-aromatic carbonate may be carried out at a wide range of temperatures ranging from 30 to 370 °C; and particularly at 150 to 320 °C, the desired aromatic carbonate compounds can be produced in high yields and selectivities.

JP-A-63023/1979 discloses that in the production of aromatic carbonates, the reaction is carried out at a temperature of 20 to 300 °C, thus suggesting a temperature range over which the process of the present invention may be carried out. However, JP-A-63023/1979 states that if the reaction temperature is too high, the catalyst will lose activity or the resulting carbonates undesirably undergo decomposition, and recommends the use of temperatures of not more than 250 °C as preferred reaction temperatures. In actual working examples in JP-A-63023/1979 the reaction was carried out at a temperature of not more than 200 °C.

In view of this fact, it is surprising that in the present invention, the reaction can be performed at a temperature of a wide range from 30 to 370 °C. As stated hereinabove, when the aromatic carbonate compounds are to be obtained by the reactions (1) and (2), the equilibrium constants of the reaction, K_1 and K_2 , are low and the rate of the reaction is low in the prior art. Hence, the yield of the desired product in the prior art is low. In order to remedy this defect of the prior art, the present inventors made extensive investigations, and found that while the equilibrium constants K_1 and K_2 are very low at a temperature of about 100 °C, they surprisingly increase abruptly as the reaction temperature is elevated, and that when the reaction is carried out at temperatures of as high as 150 to 320 °C, aromatic carbonates of high quality can be obtained in high yields and high selectivities within a short reaction time. In addition at such high temperatures, the aromatic carbonate compounds can be obtained in high yields by using the catalyst in small amounts. A further advantage is that since the amount of the catalyst is small and the desired product can be obtained within a short reaction time, side-reactions are limited, and the product is of excellent quality.

As shown in JP-A-63023/1979, when the conventional catalysts are used at elevated temperatures, a by-product ether compound $ArOR'$ (Ar and R' are as in formula (II) shown hereinafter) forms in addition to the desired aromatic carbonate compound. Furthermore, because the starting di-aliphatic carbonate or aliphatic-aromatic carbonate is decomposed, the selectivity of the aromatic carbonate undesirably decreases. The use of the catalyst specified in this invention offers the advantage that even at high reaction temperatures, the selectivity of the desired product is high, and that since the reaction solution is hardly colored and is a homogenous solution, the aromatic carbonate can be easily purified.

In the process of this invention, the mole ratio of the phenolic compound to the di-aliphatic carbonate or aliphatic-aromatic carbonate is from 5:1 to 1:5, but preferably about 1:1. The selectivity of the desired product is high, and the aromatic carbonate compound can be obtained at a high space time yield (STY) per unit volume of the reaction apparatus.

The conventional method by which the yield of the aromatic carbonate is increased involves carrying out the reaction while the resulting ROH is removed out of the reaction system, and thus shifting the equilibrium to the product side. This method can also be applied to the process of this invention. In this case, too, since the equilibrium constants K_1 and K_2 in the reaction system are higher than in the prior art, ROH can be removed by, for example, distillation with a smaller tray number, and the yield can be increased more efficiently. If $MeOCO_2Me$ is used as a material in the distillation operation $MeOH$ azeotropes with $MeOCO_2Me$. When this azeotropic mixture is separated in a distillation column and only $MeOH$ is removed, the yield of the aromatic carbonate is increased. Since in this case, the concentration of ROH becomes high owing to higher equilibrium constants K_1 and K_2 , the removal of ROH by distillation becomes easy and expenses that go into equipment and utility can be curtailed to economic advantage. ROH can be more efficiently removed from the reaction mixture if as in the prior art, an azeotropic agent such as benzene or heptane is added to the reaction system and ROH is removed as an azeotrope with the azeotropic agent.

The reaction time is 2 minutes to 10 hours, preferably 10 minutes to 3 hours, and the process of this invention is economically better than the conventional methods which require a reaction time of 8 to 24 hours on an average.

Generally, when the catalyst is other than a tin catalyst, the reaction time may vary depending upon the type and amount of the catalyst and the reaction temperature, and is 2 minutes to 40 hours, preferably 10 minutes to 3 hours. If the reaction temperature is 230 °C or higher, the equilibrium constants of the reaction, K_1 and K_2 , become high, and the reaction can be completed within a period of as short as 10 minutes to 1 hour. In this case, a product of excellent quality can be obtained in addition to the economical advantage of shortening the reaction time.

The conventional method in which to increase the yield of the aromatic carbonate, the reaction is carried out while removing ROH out of the reaction system and thus the equilibrium is shifted to the product side may also be applied to this aspect of the process of this invention. Furthermore, as in the prior art, it is possible to add an azeotropic agent such as benzene or heptane to the reaction system and remove ROH as an azeotrope with the azeotropic agent. This enables more efficient removal of ROH.

The starting compounds and the catalyst used in this invention and the products obtained will be described below in detail.

Phenolic Compound

The phenolic compounds used in this invention are represented by the following formula

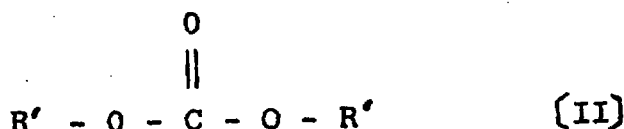


wherein Ar represents an aromatic compound residue of a substituted or unsubstituted benzene, naphthalene, anthracene or tetralin ring.

Specific examples of the phenolic compounds of formula [I] include phenol, o-, m- or p-cresol, o-, m- or p-chlorophenol, o-, m- or p-ethylphenol, o-, m- or p-(iso)propylphenol, o-, m- or p-phenoxyphenol, o-, m- or p-phenylphenol, o-, m- or p-methoxyphenol, o-, m- or p-nitrophenol, 2,6-dimethylphenol, 2,4-dimethylphenol, 3,4-dimethylphenol, 2,6-dibutylphenol, alpha-naphthol, beta-naphthol and beta-anthrol. Of these, phenol is most preferably used.

Di-aliphatic carbonates

The di-aliphatic carbonates used in this invention are represented by the following general formula

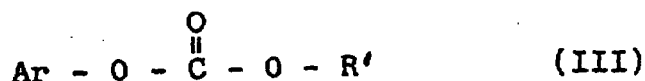


wherein R' represents a monovalent aliphatic hydrocarbon group having 1 to 12 carbon atoms, preferably an alkyl or cycloalkyl group. The two R' groups may be linked to each other. The alkyl group may be linear or branched alkyl group having 1 to 12 carbon atoms, and examples include methyl, ethyl, propyl, isopropyl, butyl, t-butyl, pentyl, neopentyl, hexyl, heptyl and octyl groups. Examples of the cycloalkyl group are cycloalkyl groups having 5 to 7 carbon atoms in the ring, and include cyclopentyl, methylcyclohexyl, cyclohexyl and cycloheptyl groups. An ethylene group may be cited as an example of two R' groups linked to each other.

Specific examples of the compounds represented by general formula [II] include dimethyl carbonate, diethyl carbonate, di-n-butyl carbonate, dicyclohexyl carbonate, dibenzyl carbonate, di-n-octyl carbonate, diisopropyl carbonate and ethylene carbonate. Of these, dimethyl carbonate is preferably used.

Aliphatic-Aromatic Carbonates

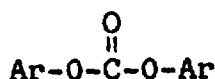
The aliphatic-aromatic carbonates used in this invention are represented by the following general formula (III)



wherein Ar is as defined in formula (I), and R' is as defined in formula (II). Specific examples include phenylmethyl carbonate, phenylethyl carbonate, phenylcyclohexyl carbonate, and tolylmethyl carbonate. Of these, phenylmethyl carbonate is preferably used when the reaction is to be carried out in the presence of the specific catalyst.

Aromatic carbonate compounds

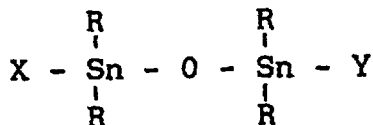
The aromatic carbonate compound as the product in this invention is an aliphatic-aromatic carbonate, a diaromatic carbonate or a mixture of both. The diaromatic carbonate is represented by the formula



wherein Ar is as defined in formula (I). Specific examples are diphenyl carbonate di(methylphenyl) carbonate, di(dimethylphenyl) carbonate and dinaphthyl carbonate.

Catalysts

(1) Tin compound catalysts are SnO and/or metal compounds of the following formula



wherein X, Y and R are as defined above. Specific examples of the metal compounds include

a (R = Bu, X = Cl, Y = Cl), b (R = Bu, X = Cl, Y = OH), c (R = Bu, X = Cl, Y = OPh), d (R = Bu, X = Br, Y = Br), e (R = Bu, X = Br, Y = OH), f (R = Bu, X = Br, Y = OPh), g (R = Bu, X = NCS, Y = NCS), h (R = Bu, X = NCS, Y = OH), i (R = Bu, X = NCS, Y = OPh), j (R = Bu, X = NCS, Y = OCH₃), k (R = Bu, X = Cl, Y = CH₂Ph), l (R = Bu, X = OAc, Y = OAc), m (R = Et, X = Cl, Y = Cl), n (R = Et, X = NCS, Y = NCS), o (R = Me, X = Cl, Y = Cl), p (R = Me, X = OAc, Y = OAc) and q (R = Ph, X = Cl, Y = Cl).

These catalysts show excellent catalyst activity even when used singly. If desired, however, they may be used in combination with each other.

(2) Catalyst comprising Sc, Cr, Mo, W, Mn, Au, Ga, In, Bi, Te and lanthanoids

This catalyst is at least one compound of an element selected from the group consisting of Sc, Cr, Mo, W, Mn, Au, Ga, In, Bi, Te and lanthanoids. Compounds of Sc, Mo, Mn, Au, Bi and lanthanoids have high catalytic activity and the desired products can be obtained in high yields.

Specific examples of such catalysts include

Sc₂O₃, Sc₂C₂, Sc(OH)₃, ScCl₃, ScF₃;

Mo(CH₃COCHCOCH₃)₃, Mo(CO)₆, Mo₂O₃, Mo(OH)₃, MoO₂, C₅H₅MoC₆H₅;

Mn₂(CO)₁₀, Mn(CH₃COCHCOCH₃)₃, MnO₂, KMnO₄, Mn₂O₇, MnCl₂;

NaAuCl₂ · 2H₂O, AuCl₃, AuF₃;

Bi(OCOCH₃)₃, BiH₃, Mg₃Bi₂;

La(OCOCH₃)₂, La(OH)₃, Ce(OH)₃, Pr(OH)₃, Nd(OH)₃, Pm(OH)₃, Sm(OH)₃, Eu(OH)₃, Gd(OH)₃, Lu(OH)₃, LuCl₃ · 6H₂O, La(NO₃)₃, La₂O₃;

Cr(CH₃COCHCOCH₃)₃, Cr(CO)₆, Cr₂O₃, Cr(OH)₃, K₂Cr₂O₇, (NH₄)₂Cr₂O₇, Cr(H₂O)₆Cl₃, CrO₃;

W(CO)₆, WO₂, WO₃, WF₆, WCl₆, WBr₆;

Ga(NO₃)₃, GaCl₂, GaCl₃;

In₂O₃, (InH₃)_n, InCl₂;

TeCl_4 , TeH_2 , TeF_6 , TeO_2 , TeCl_4 , H_2TeCl_6 and TeO .

Preferred among them are Sc_2O_3 , $\text{Mo}(\text{CH}_3\text{COCHCOCH}_3)_3$, $\text{Mo}(\text{CO})_6$, $\text{Mn}_2(\text{CO})_{10}$, $\text{Mn}(\text{CH}_3\text{COCHCOCH}_3)_3$, $\text{NaAuCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{Bi}(\text{OCOCH}_3)_3$, $\text{La}(\text{OCOCH}_3)_3$ and $\text{LuCl}_3 \cdot 6\text{H}_2\text{O}$.

These catalysts show excellent catalytic activity even when used singly. If desired, however, they may be used in combination with each other.

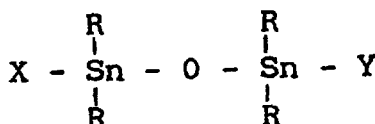
The amount of the catalyst (1) or (2) is an amount generally called a catalytic amount, which is effective for catalyzing the ester interchange reaction of the phenolic compound with the aliphatic-aromatic carbonate. It is generally used in an amount of 10 to 10^{-4} mole %, preferably 0.2 to 10^{-3} mole %, based on the amount of the phenolic compound.

Di-aromatic carbonates may be produced by heating the aliphatic-aromatic carbonate or a mixture of it with a di-aromatic carbonate obtained by the process set forth in claim 1 or 2 further in the presence of a catalyst.

The catalyst may be the same as the one used in the previous step, but may be a different catalyst selected from those described hereinabove.

This reaction is shown by the above reaction equation (3), and may be carried out at a reaction temperature of 50 to 370°C , preferably 150 to 320°C , under elevated, atmospheric or reduced pressure. Preferably, it is carried out under reduced pressure while removing the resulting di-aliphatic carbonate out of the reaction system.

Thus, by reacting the phenolic compound with the di-aliphatic carbonate or the aliphatic-aromatic carbonate in the presence of a highly active catalyst composed of SnO and/or a tin compound represented by the following formula



wherein X, Y and R are as defined above,

an aromatic carbonate can be obtained in high yields and selectivities. Since the reaction solution is not colored, it can be easily purified to obtain a pure aromatic carbonate.

Furthermore, according to this invention, an aromatic carbonate can be produced in high yields by carrying out the above reaction in the presence of a catalyst composed of at least one compound of an element selected from the group consisting of Sc, Cr, Mo, W, Mn, Au, Ga, In, Bi, Te and lanthanoids as defined in claim 1. According to this process, isolation of the product and the recovery of the catalyst can be easily performed. This advantage is greater when at least one compound of an element selected from Sc, Mo, Mn, Au, Bi and lanthanoids is used as the catalyst.

The following examples illustrate the present invention in greater detail. Examples 1 to 13 and Comparative Example 1 illustrate the use of tin-containing catalysts, and Examples 14 to 26, the use of the other type of catalysts.

Example 1

Phenol (0.11 mole), 0.11 mole of dimethyl carbonate (DMC) and 0.01 g of $\text{Cl}^n\text{Bu}_2\text{SnOSn}^n\text{Bu}_2(\text{OH})$ were put in a 50 ml. autoclave, and heated at 265°C for 30 minutes. After the reaction, the reaction solution was a yellowish nearly colorless, uniform solution. Its gas chromatographic analysis showed that the conversion of phenol was 12.46 %, the yield of phenylmethyl carbonate (PMC) based on phenol was 12.04 %, the yield of anisole was 0.42 %, and the selectivity of PMC was 96.6 %.

Examples 2-8

Example 1 was repeated except that the reaction temperature and the amounts of the starting materials and the catalyst were changed. The results are shown in Table 1.

Examples 9-12

Example 1 was repeated except that the reaction temperature and the catalyst were changed as indicated in Table 1. The results are shown in Table 1. The reaction solutions were colorless or slightly yellowish uniform solutions.

Comparative Example 1

Example 1 was repeated except that SnCl_4 was used as the catalyst and the reaction temperature was changed to 280°C . The results are shown in Table 1. The reaction solution was brown, and a black precipitate formed.

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Table 1

Example No.	Starting Materials		Catalyst Compounds	Reaction Conditions (°C/hr)	Yield of the products (based on phenol, %)			Conversion of phenol (%)	Selectivity of PMC + DPC (%)
	phenol	DMC			anisole	PMC	DPC ¹		
1	0.11	0.11	Cl ⁿ Bu ₂ SnOSn ⁿ Bu ₂ (OH)	265/0.5	0.42	12.04	0	12.46	96.6
2	0.11	0.11	Cl ⁿ Bu ₂ SnOSn ⁿ Bu ₂ (OH)	200/0.5	0	5.32	0	5.32	100
3	0.11	0.11	Cl ⁿ Bu ₂ SnOSn ⁿ Bu ₂ (OH)	225/0.5	0.19	6.92	0	7.10	97.3
4	0.11	0.11	Cl ⁿ Bu ₂ SnOSn ⁿ Bu ₂ (OH)	250/0.5	0.11	11.70	0	11.81	99.1
5	0.11	0.11	Cl ⁿ Bu ₂ SnOSn ⁿ Bu ₂ (OH)	280/0.5	1.11	14.94	0	16.05	93.1
6	0.11	0.11	Cl ⁿ Bu ₂ SnOSn ⁿ Bu ₂ (OH)	298/0.5	1.13	15.16	1.20	20.33	80.5
7	0.11	0.11	Cl ⁿ Bu ₂ SnOSn ⁿ Bu ₂ (OH)	353/0.5	7.80	14.12	3.61	32.90	53.9
8	0.11	0.05	Cl ⁿ Bu ₂ SnOSn ⁿ Bu ₂ (OH)	283/0.5	1.34	7.75	0	9.09	85.3
9	0.11	0.11	SnO	250/0.5	0.16	12.52	0.70	13.38	98.8
10	0.11	0.11	Cl ⁿ Bu ₂ SnOSn ⁿ Bu ₂ Cl	250/0.5	0.10	12.76	0.52	13.38	99.3
11	0.11	0.11	(NCS) ⁿ Bu ₂ SnOSn ⁿ -Bu ₂ (OCH ₃)	250/0.5	0.10	12.70	0.30	13.10	99.2
12	0.11	0.11	(CH ₃ CO ₂) ⁿ Bu ₂ SnO-Sn ⁿ Bu ₂ (OCCH ₃)	250/0.5	0.11	11.60	0	11.71	99.1
Comparative Example 1	0.11	0.11	SnCl ₄	280/0.5	4.88	10.82	0	15.70	68.9

1) DPC = diphenyl carbonate, 2) ⁿBu: normal butyl

Example 13

Phenylmethyl carbonate (7 millimoles) and 0.01 g of ClⁿBu₂SnOⁿBu₂(OH) were heated in an autoclave at 200 °C for 1 hour. Analysis of the reaction solution by gas chromatography showed that 1.8 millimoles of

diphenyl carbonate and 1.8 millimoles of dimethyl carbonate formed.

Example 14

5 Phenol (0.11 mole), 0.11 mole of dimethyl carbonate and 0.01 g of $\text{Mn}_2(\text{CO})_{10}$ were put in a 50 ml. autoclave, and heated at 250°C for 30 minutes. Gas chromatographic analysis of the reaction solution showed that the conversion of phenol was 15.17 % and anisole, phenylmethyl carbonate (PMC) and diphenyl carbonate (DPC) formed in a yield of 1.78 %, 12.50 %, and 0.89 %, respectively, based on phenol. The total selectivity of PMC and DPC was 88.3 %.

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Examples 15-25

Example 14 was repeated except that the catalysts indicated in Table 2 were used instead of the catalyst used in Example 14. The results are shown in Table 2.

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Example 26

Phenylmethyl carbonate (7 millimole) and 0.01 g of $\text{Mn}_2(\text{CO})_{10}$ were heated in an autoclave at 200°C for 1 hour. Gas chromatographic analysis of the reaction solution showed that 1.7 millimoles of diphenyl carbonate and 1.7 millimoles of dimethyl carbonate formed.

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Table 2

Example No.	Catalyst	Yields of the products (based on phenol, %)			Conversion of phenol (%)	Selectivity of PMC + DPC (%)
		anisole	PMC	DMC		
14	$\text{Mn}(\text{CO})_{10}$	1.78	12.50	0.89	15.17	88.3
15	Sc_2O_3	0.37	7.24	0	7.63	95.1
16	$\text{Mo}(\text{CH}_3\text{COCHCOCH}_3)_3$	0.21	7.68	0	7.89	97.3
17	$\text{NaAuCl}_2 \cdot 2\text{H}_2\text{O}$	4.12	7.93	0	12.03	65.8
18	$\text{Bi}(\text{OCOCH}_3)_3$	0.45	7.67	0.40	8.52	94.7
19	$\text{La}(\text{OCOCH}_3)_2 \cdot 1.5\text{H}_2\text{O}$	2.92	8.34	0	11.26	74.1
20	$\text{LuCl}_3 \cdot 6\text{H}_2\text{O}$	1.91	11.02	0.67	13.60	86.0
21	$\text{Cr}(\text{CH}_3\text{COCHCOCH}_3)_3$	0.36	3.00	0	3.36	89.3
22	$\text{W}(\text{CO})_6$	0.31	3.39	0	3.70	91.6
23	$\text{Ga}(\text{NO}_3)_3 \cdot \text{H}_2\text{O}$	0.21	4.54	0	4.75	95.6
24	In_2O_3	0.42	3.72	0	4.14	89.9
25	TeCl_4	0.17	3.04	0	3.21	94.7

Claims

1. A process for producing an aromatic carbonate compound selected from aliphatic-aromatic carbonates, di-aromatic carbonates and mixtures of these, which comprises reacting a phenolic compound represented by formula (I)

Table 2

Example No.	Catalyst	Yields of the products (based on phenol, %)			Conversion of phenol (%)	Selectivity of PMC + DPC (%)
		anisole	PMC	DMC		
14	$Mn(CO)_5$	1.78	12.50	0.89	15.17	88.3
15	Sc_2O_3	0.37	7.24	0	7.63	95.1
16	$Mo(CH_3COCHCOCH_3)_3$	0.21	7.68	0	7.89	97.3
17	$NaAuCl_2 \cdot 2H_2O$	4.12	7.93	0	12.03	65.8
18	$Bi(OCOCH_3)_3$	0.45	7.67	0.40	8.52	94.7
19	$La(OCOCH_3)_2 \cdot 1.5H_2O$	2.92	8.34	0	11.26	74.1
20	$LuCl_3 \cdot 6H_2O$	1.91	11.02	0.67	13.60	86.0
21	$Cr(CH_3COCHCOCH_3)_3$	0.36	3.00	0	3.36	89.3
22	$W(CO)_6$	0.31	3.39	0	3.70	91.6
23	$Ga(NO_3)_3 \cdot H_2O$	0.21	4.54	0	4.75	95.6
24	In_2O_3	0.42	3.72	0	4.14	89.9
25	$TeCl_4$	0.17	3.04	0	3.21	94.7

Claims

1. A process for producing an aromatic carbonate compound selected from aliphatic-aromatic carbonates, di-aromatic carbonates and mixtures of these, which comprises reacting a phenolic compound represented by formula (I)



ArOH (I)

where Ar represents an aromatic compound residue of a substituted or unsubstituted benzene, naphthalene, anthracene or tetralin ring with a di-aliphatic carbonate compound represented by formula (II)



where R' represents a monovalent aliphatic hydrocarbon group having 1 to 12 carbon atoms and the two R' may link each other to form an alicyclic ring or an aliphatic-aromatic carbonate represented by formula (III)



wherein Ar is as defined in formula (I) and R' is a monovalent aliphatic hydrocarbon group have 1 to 12 carbon atoms in the presence of a catalyst selected from

Sc₂O₃, ScC₂, Sc(OH)₃, ScCl₃, ScF₃;

Mo(CH₃COCHCOCH₃)₃, Mo(CO)₆, Mo₂O₃, Mo(OH)₃, MoO₂, C₅H₅MoC₆H₅;

Mn₂(CO)₁₀, Mn(CH₃COCHCOCH₃)₃, MnO₂, KMnO₄, Mn₂O₇, MnCl₂;

NaAuCl₂·2H₂O, AuCl₃, AuF₃;

Bi(OCOCH₃)₃, BiH₃, Mg₃Bi₂;

La(OCOCH₃)₂, La(OH)₃, Ce(OH)₃, Pr(OH)₃, Nd(OH)₃, Pm(OH)₃, Sm(OH)₃, Eu(OH)₃, Gd(OH)₃, Lu(OH)₃,

LuCl₃·6H₂O, La(NO₃)₃, La₂O₃;

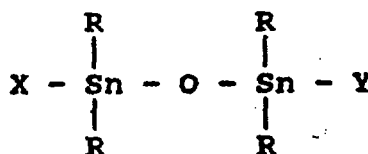
Cr(CH₃COCHCOCH₃)₃, Cr(CO)₆, Cr₂O₃, Cr(OH)₃, K₂Cr₂O₇, (NH₄)₂Cr₂O₇, Cr(H₂O)₆Cl₃, CrO₃;

W(CO)₆, WO₂, WO₃, WF₆, WCl₆, WBr₆;

Ga(NO₃)₃, GaCl₂, GaCl₃;

In₂O₃, (InH₃)_n, InCl₂;

TeCl₄, TeH₂, TeF₆, TeO₂, TeCl₄, H₂TeCl₆, TeO, SnO and/or a tin compound represented by the following formula



wherein X and Y are identical or different and each represents OH, SCN, OR¹, OCOR¹ or a halogen atom, R¹ represents an alkyl or aryl group, R represents an alkyl or aryl group, with the proviso that X and Y are not simultaneously OR¹.

2. A process according to claim 1 in which the reaction is carried out at a temperature of 150 to 320 °C.
3. A process according to claim 1 or 2 in which the mole ratio of the phenolic compound to the di-aliphatic carbonate or aliphatic-aromatic carbonate is from 5:1 to 1:5.
4. A process according to claim 1, 2 or 3 in which the catalyst is used in a concentration of 0.2 mole % to 10⁻³ mole % based on the phenolic compound.



5. A process according to any one of the preceding claims in which the phenolic compound is phenol.
6. A process according to any one of the preceding claims in which the di-aliphatic carbonate is dimethyl carbonate.
7. A process according to any one of the preceding claims in which the aliphatic-aromatic carbonate is methylphenyl carbonate.
8. A process according to any one of the preceding claims in which the catalyst is at least one compound selected from
 Sc_2O_3 , ScCl_2 , $\text{Sc}(\text{OH})_3$, ScCl_3 , ScF_3 ;
 $\text{Mo}(\text{CH}_3\text{COCHCOCH}_3)_3$, $\text{Mo}(\text{CO})_6$, Mo_2O_3 , $\text{Mo}(\text{OH})_3$, MoO_2 , $\text{C}_5\text{H}_5\text{MoC}_6\text{H}_5$;
 $\text{Mn}_2(\text{CO})_{10}$, $\text{Mn}(\text{CH}_3\text{COCHCOCH}_3)_3$, MnO_2 , KMnO_4 , Mn_2O_7 , MnCl_2 ;
 $\text{NaAuCl}_2 \cdot 2\text{H}_2\text{O}$, AuCl_3 , AuF_3 ;
 $\text{Bi}(\text{OCOCH}_3)_3$, BiH_3 , Mg_3Bi_2 ;
 $\text{La}(\text{OCOCH}_3)_2$, $\text{La}(\text{OH})_3$, $\text{Ce}(\text{OH})_3$, $\text{Pr}(\text{OH})_3$, $\text{Nd}(\text{OH})_3$, $\text{Pm}(\text{OH})_3$, $\text{Sm}(\text{OH})_3$, $\text{Eu}(\text{OH})_3$, $\text{Gd}(\text{OH})_3$, $\text{Lu}(\text{OH})_3$,
 $\text{LuCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{La}(\text{NO}_3)_3$ and La_2O_3 .
9. A process for producing a di-aromatic carbonate, which comprises heating the aliphatic-aromatic carbonate of formula III according to claim 1 or a mixture of it with a di-aromatic carbonate obtained by the process of any one of the preceding claims in the presence of a catalyst as defined in claim 1.

Patentansprüche

1. Verfahren zur Herstellung einer aromatischen Carbonatverbindung, ausgewählt aus aliphatisch/aromatischen Carbonaten, diaromatischen Carbonaten und Gemischen davon, umfassend die Umsetzung einer phenolischen Verbindung, angegeben durch die Formel (I)



in der Ar einen Rest einer aromatischen Verbindung eines substituierten oder unsubstituierten Benzol-, Naphthalin-, Anthracen- oder Tetralinrings bedeutet, mit einer dialiphatischen Carbonatverbindung, angegeben durch die Formel (II)



in der R' eine einwertige aliphatische Kohlenwasserstoffgruppe mit 1 bis 12 Kohlenstoffatomen bedeutet und die beiden Reste R' miteinander verbunden sein können unter Bildung eines alicyclischen Rings oder einem aliphatisch/aromatischen Carbonat, angegeben durch die Formel (III)



wobei Ar wie bei Formel (I) definiert ist und R' eine einwertige aliphatische Kohlenwasserstoffgruppe mit 1 bis 12 Kohlenstoffatomen bedeutet, in Gegenwart eines Katalysators, ausgewählt aus

Sc_2O_3 , ScCl_2 , $\text{Sc}(\text{OH})_3$, ScCl_3 , ScF_3 ;
 $\text{Mo}(\text{CH}_3\text{COCHCOCH}_3)_3$, $\text{Mo}(\text{CO})_6$, Mo_2O_3 , $\text{Mo}(\text{OH})_3$, MoO_2 , $\text{C}_5\text{H}_5\text{MoC}_6\text{H}_5$;
 $\text{Mn}_2(\text{CO})_{10}$, $\text{Mn}(\text{CH}_3\text{COCHCOCH}_3)_3$, MnO_2 , KMnO_4 , Mn_2O_7 , MnCl_2 ;
 $\text{NaAuCl}_2 \cdot 2\text{H}_2\text{O}$, AuCl_3 , AuF_3 ;
 $\text{Bi}(\text{OCOCH}_3)_3$, BiH_3 , Mg_3Bi_2 ;
 $\text{La}(\text{OCOCH}_3)_2$, $\text{La}(\text{OH})_3$, $\text{Ce}(\text{OH})_3$, $\text{Pr}(\text{OH})_3$, $\text{Nd}(\text{OH})_3$, $\text{Pm}(\text{OH})_3$, $\text{Sm}(\text{OH})_3$, $\text{Eu}(\text{OH})_3$, $\text{Gd}(\text{OH})_3$, $\text{Lu}(\text{OH})_3$,



LuCl₃·6H₂O, La(NO₃)₃, La₂O₃;

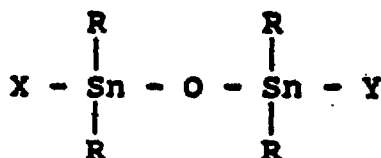
Cr(CH₃COCHCOCH₃)₃, Cr(CO)₆, Cr₂O₃, Cr(OH)₃, K₂Cr₂O₇, (NH₄)₂Cr₂O₇, Cr(H₂O)₆Cl₃, CrO₃;

W(CO)₆, WO₂, WO₃, WF₆, WCl₆, WBr₆;

Ga(NO₃)₃, GaCl₃, GaCl₂, GaCl₃;

6 In₂O₃, (InH₃)_n, InCl₂;

TeCl₄, TeH₂, TeF₆, TeO₂, TeCl₄, K₂TeCl₆, TeO, SnO und/oder einer Zinnverbindung, angegeben durch die folgende Formel



15 wobei X und Y gleich oder verschieden sind und jeweils OH, SCN, OR¹, OCOR¹ oder ein Halogenatom bedeuten, R¹ eine Alkyl- oder Arylgruppe ist, R eine Alkyl- oder Arylgruppe ist, mit der Maßgabe, daß X und Y nicht gleichzeitig OR¹ sind.

20 2. Verfahren nach Anspruch 1, wobei die Reaktion bei einer Temperatur von 150 bis 320 °C durchgeführt wird.

3. Verfahren nach Anspruch 1 oder 2, wobei das Molverhältnis von phenolischer Verbindung zu dem dialiphatischen Carbonat oder aliphatisch/aromatischen Carbonat 5:1 bis 1:5 beträgt.

4. Verfahren nach Anspruch 1, 2 oder 3, wobei der Katalysator in einer Konzentration von 0,2 mol-% bis 10⁻³ mol-%, bezogen auf die phenolische Verbindung, angewandt wird.

5. Verfahren nach einem der vorangehenden Ansprüche, wobei die phenolische Verbindung Phenol ist.

6. Verfahren nach einem der vorangehenden Ansprüche, wobei das dialiphatische Carbonat Dimethylcarbonat ist.

7. Verfahren nach einem der vorangehenden Ansprüche, wobei das aliphatisch/aromatische Carbonat Methylphenylcarbonat ist.

8. Verfahren nach einem der vorangehenden Ansprüche, wobei der Katalysator mindestens eine Verbindung ist, ausgewählt aus

Sc₂O₃, ScCl₂, Sc(OH)₃, ScCl₃, ScF₃;

Mo(CH₃COCHCOCH₃)₃, Mo(CO)₆, Mo₂O₃, Mo(OH)₃, MoO₂, C₅H₅MoC₆H₅;

Mn₂(CO)₁₀, Mn(CH₃COCHCOCH₃)₃, MnO₂, KMnO₄, Mn₂O₇, MnCl₂;

NaAuCl₂·2H₂O, AuCl₃, AuF₃;

Bi(OCOCH₃)₃, BiH₃, Mg₃Bi₂;

La(OCOCH₃)₂, La(OH)₃, Ce(OH)₃, Pr(OH)₃, Nd(OH)₃, Pm(OH)₃, Sm(OH)₃, Eu(OH)₃, Gd(OH)₃, Lu(OH)₃, LuCl₃·6H₂O, La(NO₃)₃ und La₂O₃.

9. Verfahren zur Herstellung eines diaromatischen Carbonats, umfassend das Erhitzen des aliphatisch/aromatischen Carbonats der Formel (III) nach Anspruch 1 oder eines Gemisches davon mit einem diaromatischen Carbonat, das erhalten worden ist nach dem Verfahren nach einem der vorangehenden Ansprüche, in Gegenwart eines Katalysators, wie in Anspruch 1 definiert.

Revendications

1. Procédé de préparation d'un carbonate aromatique choisi parmi les carbonates aliphatique-aromatiques, diaromatiques et les mélanges de ceux-ci, lequel procédé comprend la réaction d'un composé phénolique représenté par la formule (I)



(I) ArOH

dans laquelle Ar représente un résidu d'un composé aromatique, tel que le benzène, le naphthalène, l'anthracène ou la tétraline, substitués ou non, avec un composé de type carbonate dialiphatique représenté par la formule (II)



dans laquelle R' représente un groupe hydrocarboné aliphatique monovalent comportant de 1 à 12 atomes de carbone et les deux R' peuvent être liés l'un à l'autre pour former un cycle alicyclique, ou un carbonate aliphatique-aromatique représenté par la formule (III)



dans laquelle Ar est défini comme dans la formule (I) et R' est un groupe hydrocarboné aliphatique monovalent comportant de 1 à 12 atomes de carbone, en présence d'un catalyseur choisi parmi

Sc₂O₃, ScC₂, Sc(OH)₃, ScCl₃, ScF₃,

Mo(CH₃COCHCOCH₃)₃, Mo(CO)₆, Mo₂O₃, Mo(OH)₃, MoO₂, C₅H₅MoC₆H₅,

Mn₂(CO)₁₀, Mn(CH₃COCHCOCH₃)₃, MnO₂, KMnO₄, Mn₂O₇, MnCl₂,

NaAuCl₂.2H₂O, AuCl₃, AuF₃,

Bi(OCOCH₃)₃, BiH₃, Mg₃Bi₂,

La(OCOCH₃)₂, La(OH)₃, Ce(OH)₃, Pr(OH)₃, Nd(OH)₃, Pm(OH)₃,

Sm(OH)₃, Eu(OH)₃, Gd(OH)₃, Lu(OH)₃, LuCl₃.6H₂O, La(NO₃)₃, La₂O₃,

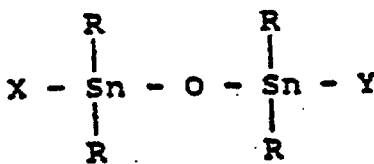
Cr(CH₃COCHCOCH₃)₃, Cr(CO)₆, Cr₂O₃, Cr(OH)₃, K₂Cr₂O₇, (NH₄)₂Cr₂O₇, Cr(H₂O)₆Cl₃, CrO₃,

W(CO)₆, WO₂, WO₃, WF₆, WCl₆, WBr₆,

Ga(NO₃)₃, GaCl₂, GaCl₃,

InO₃, (InH₃)_n, InCl₂,

TeCl₄, TeH₂, TeF₆, TeO₂, TeCl₄, H₂TeCl₆, TeO, SnO et/ou un composé d'étain correspondant à la formule



dans laquelle X et Y sont identiques ou différents et représentent chacun un résidu OH, SCN, OR', OCOR' ou un atome d'halogène, R' représente groupe alkyle ou aryle, R représente un groupe alkyle ou aryle, à condition que X et Y ne représentent pas simultanément un groupe OR.

2. Procédé conforme à la revendication 1 dans lequel la réaction est réalisée à une température comprise entre 150 et 320 °C.
3. Procédé conforme à la revendication 1 ou 2 dans lequel le rapport molaire du composé phénolique au carbonate dialiphatique ou aliphatique-aromatique est compris entre 5/1 et 1/5.
4. Procédé conforme à la revendication 1, 2 ou 3 dans lequel le catalyseur est utilisé en une concentration de 0,2 % en moles à 10⁻³ % en moles par rapport au composé phénolique.



5. Procédé conforme à une quelconque des revendications précédentes dans lequel le composé phénolique est le phénol.
6. Procédé conforme à une des revendications précédentes dans lequel le carbonate dialiphatique est le carbonate de diméthyle.
7. Procédé conforme à une quelconque des revendications précédentes dans lequel le carbonate aliphatique-aromatique est le carbonate de méthyle et de phényle.
8. Procédé conforme à une quelconque des revendications précédentes dans lequel le catalyseur est au moins un composé choisi parmi
 Sc_2O_3 , ScC_2 , $\text{Sc}(\text{OH})_3$, ScCl_3 , ScF_3 ,
 $\text{Mo}(\text{CH}_3\text{COCHCOCH}_3)_3$, $\text{Mo}(\text{CO})_6$, Mo_2O_3 , $\text{Mo}(\text{OH})_3$, MoO_2 , $\text{C}_5\text{H}_5\text{MoC}_5\text{H}_5$,
 $\text{Mn}_2(\text{CO})_{10}$, $\text{Mn}(\text{CH}_3\text{COCHCOCH}_3)_3$, MnO_2 , KMnO_4 , Mn_2O_7 , MnCl_2 ,
 $\text{NaAuCl}_2 \cdot 2\text{H}_2\text{O}$, AuCl_3 , AuF_3 ,
 $\text{Bi}(\text{OCOCH}_3)_3$, BiH_3 , Mg_3Bi_2 ,
 $\text{La}(\text{OCOCH}_3)_2$, $\text{La}(\text{OH})_3$, $\text{Ce}(\text{OH})_3$, $\text{Pr}(\text{OH})_3$, $\text{Nd}(\text{OH})_3$, $\text{Pm}(\text{OH})_3$,
 $\text{Sm}(\text{OH})_3$, $\text{Eu}(\text{OH})_3$, $\text{Gd}(\text{OH})_3$, $\text{Lu}(\text{OH})_3$, $\text{LuCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{La}(\text{NO}_3)_3$ et La_2O_3 .
9. Procédé de préparation d'un carbonate diaromatique qui comprend le chauffage du carbonate aliphatique-aromatique de formule III conforme à la revendication 1 ou un mélange de celui-ci avec un carbonate diaromatique obtenu par le procédé conforme à une quelconque des revendications précédentes, en présence d'un catalyseur conforme à la revendication 1.

