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(19)

(54) PREPARATION OF AROMATIC SALICYLATES

(71) We, GENERAL ELECTRIC COMPANY, a corporation organized and existing under the laws of the laws of the State of New York, United States of America, of 1 River Road, Schenectady 12305, State of New York, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:-

The present invention relates to aromatic salicylates and in particular to a process for making an aromatic silicylate.

This invention is related to those described and claimed in our co-pending British Patent Applications No. 141324/77, Serial No. 1572291; 41325/77, Serial No. 1572292; 41326/77, Serial No. 1572293; and 41327/77, Serial No. 1572294.

As is broadly disclosed in British patent applications, No. 41326/77 and 41327/77 aromatic carbonates can be prepared by contacting a phenol, carbon monoxide, a base, and a Group VIIIB element selected from ruthenium, rhodium, palladium, osmium, iridium or platinum having an oxidation state greater than zero. Those applications do not disclose, however, that, under some process conditions, not only are aromatic carbonates formed but also aromatic salicylates.

This invention provides a process for preparing an aromatic salicylate comprising forming a mixture from a phenol, carbon monoxide, and a Group VIIIB element selected from ruthenium, rhodium, palladium, osmium, iridium or platinum, adding a base to the resulting mixture within a period of up to 120 minutes from formation of the mixture, and recovering at least a portion of an aromatic salicylate.

The reactants and the resulting reaction products of the process can be illustrated by the following general equations which are furnished for illustrative purposes only since the reaction mechanisms involved in the preparation of aromatic salicylates (Eq. 1) may be much more complex.

Eq. 1

$$PdCl_2 + 2R'OH + 2R_3N + CO$$

$$\longrightarrow Pd^{o} + HO\text{-}R''\text{-}\underset{\displaystyle O}{\overset{\displaystyle \|}{C}}\text{-}O\text{-}R' + 2R_3NHCl$$

wherein R is an alkyl radical (including cycloalkyl), R′ is an aryl radical, and R″ is an arylene radical.

Any of the phenols -- subject to the proviso that the phenol have at least one *ortho*-positioned hydrogen atom relative to an -OH radical attached directly to an aromatic ring carbon atom, solvents, bases, ligands, the Group VIIIB elements, oxidants including oxygen and redox agents disclosed in the above-mentioned British Patent applications No. 41324/77 Serial Nos. 1572291; and 41327/77 Serial No. 1572294 can be employed in the process in any of the amounts disclosed relative to the aforementioned phenols, solvents, etc., as well as the reaction parameters relative to time, temperature and pressure, except, of course, as the recovery of an aromatic silicylate may require modifications thereof.

To optimize the yield of aromatic salicylate the addition of carbon monoxide is delayed until the phenolic reactant, Group VIIIB elements and base, have formed a salicylate preliminary reaction admixture, i.e. "salicylate PRM".

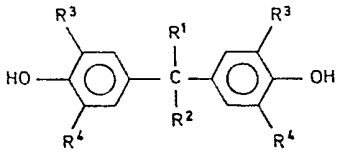
Preferably, the phenolic reaction is contacted with a Group VIIIB element having an oxidation state of at least +2 with a base prior to contacting a previously formed resulting "salicylate PRM" with carbon monoxide. In addition, it is preferred that the process is carried out under reaction conditions which exclude from the reaction media halides, i.e. chloride, bromide, iodide, or fluoride, in amounts which are in excess of the amount theoretically required to form a Group VIIIB metal halide salt.

The preference of delaying the introduction or addition of halides and/or carbon monoxide to a "salicylate PRM" until formation of the "salicylate PRM" is a result of the finding that the order of addition and type of reactants employed in the process significantly affects the formation of aromatic salicylates. The significance of the order of addition further exemplified when this disclosure is read in conjunction with the disclosure of previously mentioned British patent application No. 41325/77, Serial No. 1572292.

Preferred phenolic reactants are phenols containing from 6 to 30, and more preferably from 6 to 15, carbon atoms. Illustrative of commercially important phenolic reactants included within the above description are the following: phenol itself (hydroxy benzene); napthol; *ortho*-, *meta*-, or *para*cresol; catechol; *meta*, or *para*-xylenol; resorcinol; the various isomers of dihydroxydiphenyl; the isomers of dihydroxynapthalene; bis(4-hydroxyphenyl)propane-2,2; α,α′-bis(4-hydroxyphenyl)-p-diiso-propylbenzene; 4,4′-dihydroxy-3,5,3′-trichlorophenylpropane-2,2; 4,4′-dihydroxy-3,5,3′-tribomophenylpropane-2,2; phloroglucinol, and dihydroxy oligomers, for example an oligomer derived from bisphenol-A.

A generally preferred bisphenol that can be used in the process can be described by the following formula:

I.



where R^1 and R^2 are hydrogen, C_{1-4} alkyl or phenyl, and at least one of R^3 or R^4 is hydrogen. Another preferred bisphenol comprises formula I where R^1 and R^2 are as defined before and at least one of R^3 is hydrogen and the other is hydrogen or C_{1-4} alkyl, and at least one of R^4 is hydrogen and the other is hydrogen or C_{1-4} alkyl. Especially preferred is bis(4-hydroxy-phenyl)propane-2,2, also commonly known as "bisphenol-A" (BPA).

Illustrative of the generally preferred Group VIIIB element compounds or complexes that can be used in the process follow: $RuCl_2$, $RuBr_2$, RuI_2, $Ru(CO)_2CI_2$, $Ru(CO)_2I_2$, $Ru(CO)_4Cl_2$, $Ru(CO)_4Br_2$, $Ru(CO)_4I_2$, $RuCl_3$, $RuBr_3$, RuI_3; $PdCl_2$, $PdBr_2$, PdI_2, $[Pd(CO)Cl_2]_2$, $[Pd(CO)Br_2]_2$, $[Pd(CO)I_2]_2$, $(C_6H_5CN)_2PdCl_2$, $PdCl_4$, $Pd(OH)_2(CNC_4H_9)_2$, $PdI_2(CNC_6H_5)_2$, $Pd(OH)_2(CNCH_3OC_6H_5)_2$, $Pd(CNC_4H_9)_4$; $Rh(CO)Cl_2$, $Rh(CO)Br_2$, $Rh(CO)I_2$, $Rh_2Cl_2(CO)_2$, $Rh_2(CO)_4Cl_2$, $Rh_2(CO)_4Br_2$, $Rh_2(CO)_4I_2$, $[Rh(CO)_2Cl]_2$, $RhCl_3$, $RhBr_3$, RhI_3; $Os(CO)_3Cl_2$, $Os(CO)_3Br_2$, $Os(CO)_3I_2$, $Os(CO)_4Cl_2$, $Os(CO)_4Br_2$, $Os(CO)_4I_2$, $Os(CO)_8Cl_2$, $Os(CO)_8Br_2$, $Os(CO)_8I_2$, $OsCl_2$, $OsCl_3$, OsI_2, OsI_3, $OsBr_3$, $OsBr_4$ and $OsCl_4$; $IrCl_3$, $IrCl_3(CO)$, $Ir_2(Co)_8$, $IrCl_3$, $IrBr_3$, $IrCl_3$, $IrBr_4$, IrI_4, $PtCl_2$, $PtBr_2$, PtI_2, $Pt(CO)_2Cl_2$, $Pt(CO)_2Br_2$, $Pt(CO)_2I_2$, $Pt(CO)_2$-Cl_4, $Pt(CO)_2Br_4$, $Pt(CO)_2I_4$, $Pt(CO)_3Cl_4$, $Pt(CO)_3Br_4$, $Pt(CO)_3I_4$, and $PtCl_2(CNC_6H_5)$.

Preferred bases are sterically hindered amines, e.g. diisopropylmonoethylamine, and 2,2,6,6,N-pentamethylpiperidine.

In the process any amount of base can be employed. In general, effective mole ratios of base to the Group VIIIB elements are within the range of from 0.00001:1 to 100:1 or higher, preferably from 0.5:1 to 10:1, and more preferably from 1:1 to 2:1. Generally, when the process is carried out in accord with any of the preferred process parameters described herein before, mole ratios of at least 1:1 enhance both the reaction rate and the yield of aromatic salicylate.

In the process, presently preferred carbon monoxide pressures are within the range of from 1 to 200 atmospheres.

In the process the molar proportions of solvent, preferably inert, to phenolic reactant are preferably from 50:50 to 99:1.

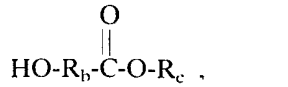
Any reaction temperature can be employed. In general, optimum reaction temperatures are 0° C., or even lower to 300° C., or even higher.

In still another process parameter of the invention, the process is carried out under catalytic reaction conditions employing an oxidant including oxygen, a redox agent and a dehydrating agent at reaction temperatures in excess of 100° C., more preferably 150° C.

and even more preferred 200° C., since optimum yields of aromatic salicylate are obtained under these reaction conditions. The oxidants, redox agents and dehydrating agents that can be used under the aforementioned preferred reaction conditions are described in detail in the above-mentioned British Patent Applications No. 41324/77 Serial No. 1572291 and 41327/77 Serial No. 1572294. Particularly preferred in the preparation of aromatic salicylates at elevated temperatures is the use of an oxidant selected from manganese or cobalt complexes and molecular sieve drying agents.

In the process whenever either air or gaseous oxygen is employed, preferably pressures within the range of from 1/2 to 200 atmospheres are employed.

The aromatic salicylates obtained according to the invention can be generically described by the following formula:



wherein R_b represents an aromatic radical wherein the hydroxyl radical is positioned *ortho*-relative to the carboxylate, i.e.

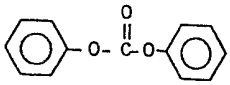
radical, and R_c represents an aromatic radical. The R_b and R_c radicals can be carbo- or hetero-monocyclic, polycyclic, or fused polycyclic, and can have two or more cyclic systems (monocyclic, polycyclic or fused polycyclic systems) which are directly joined to each other by single or double valence bonds, or by bi- or multivalent radicals.

In order that those skilled in the art may better understand the invention, the following Examples are given which are illustrative of the best mode of this invention, however, these Examples are not intended to limit the invention in any manner whatsoever. In the Examples, unless otherwise specified, all parts are by weight and the reaction products were verified by infrared spectrum, C-13 nuclear magnetic resonance and mass spectrometry.

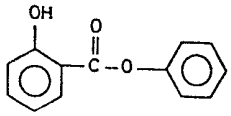
Example 1

Preparation of phenyl salicylate using hydroxybenzene carbon monoxide, diisopropylmonoethylamine and bis(benzonitrile)-palladium(II) dichloride.

A reaction vessel was charged with 1.50 g. (4.0 mml.) of bis(benzonitrile)palladium(II) dichloride, 0.77 g. (8.0 mmol.) of phenol, and 10 ml. of methylene chloride. The mixture was stirred, flushed slowly with carbon monoxide, and 1.5 g. (11.6 mmol.) of diisopropylmonoethylamine was immediately added. The solution immediately turned black and palladium metal precipitated. After stirring at room temperature for three hours, the mixture was filtered. The precipitate was washed with methylene chloride, then dried in a stream of air, to yield 0.43 g. (101%) of palladium metal. The filtrate was analyzed and the presence of 0.23 g. (52% yield) of diphenyl carbonate and 0.45 g. (53%) of phenyl salicylate of the formulae, respectively, was formed:



and



Example II

Preparation of 4'-methylphenyl-2-hydroxy-5-methyl benzoate under pressure.

The reaction medium contained 4.03 g. (1.05 mmol.) of bis(benzonitrile)palladium(II) dichloride, 20 ml. of methylene chloride, 0.108 g. of 4-methylphenol, 1.131 g. of diisopropylmonoethylamine, and sufficient carbon monoxide to charge the vessel to 65 psi. The product yield was 38% of 4,4'-dimethyldiphenyl carbonate and 41% of 4'-

methylphenyl-2-hydroxy-5-methyl benzoate.

Example III

Preparation of 4'-methylphenyl-2-hydroxy-5-methyl benzoate using palladium(II) dichloride.

A reaction vessel was charged with 10 ml. of methylene chloride, 0.108 g. (1.0 mmol.) of 4-methylphenol, 0.137 g. (1.1 mmol.) of diisopropylmonoethylamine, and sufficient carbon monoxide to pressure the vessel to 65 psi. 0.199 g. (1.12 mmol.) of palladium(II) dichloride, i.e. $PdCl_2$, was added. The product yield was 0.98 g. (81% of 4,4'-dimethyldiphenyl carbonate and 0.08 g (7%) of 4'-methylphenyl-2-hydroxy-5-methyl benzoate.

Example IV

Preparation of 4'-methylphenyl-2-hydroxy-5-methyl benzoate using 4-methyl sodium phenoxide as the base.

The reaction vessel contained 0.184 g. (1.04 mmol.) of palladium(II) dichloride, 10 ml. of methylene chloride, 0.125 g. (1.16 mmol.) of 4-methylphenol, 0.080 g. (0.62 mmol.) of 4-methyl sodium phenoxide and sufficient carbon monoxide to charge the vessel to 63 psi. The product yield was 5% of 4,4'-dimethyldiphenyl carbonate and 8% of 4'-methylphenyl-2-hydroxy-5-methyl benzoate.

Example V

Preparation of 4'-methylphenyl-2-hydroxy-5-methyl benzoate using potassium carbonate as a base.

The reaction vessel contained 0.182 g. (1.03 mmol.) of palladium(II) dichloride, 10 ml. of methylene chloride, 0.233 g. (2.16 mmol.) of 4-methylphenol, 0.320 g. (2.32 mmol.) of potassium carbonate and sufficient carbon monoxide to charge the vessel to 64 psi. The product yield was 5% of 4,4'-dimethyldiphenyl carbonate and 1% of 4'-methylphenyl-2-hydroxy-5-methyl benzoate.

Example VI

Preparation of 4'-methylphenyl-2-hydroxy-5-methyl benzoate using potassium fluoride as a base.

The reaction vessel contained 0.182 g. (1.00 mmol.) of palladium(II) dichloride, 10 ml. of methylene chloride, 0.248 g. (2.3 mmol.) of 4-methylphenol, 0.150 g. (2.6 mmol.) of potassium fluoride, and sufficient carbon monoxide to charge the vessel to 65 psi. The product yield was 3% of 4,4'-dimethyldiphenyl carbonate and 1% of 4'-methylphenyl-2-hydroxy-5-methyl benzoate.

Example VII

Preparation of phenyl salicylate using rhodium(III) trichloride.

A reaction vessel was charged with 4 g. (42.0 mmol.) of hydroxybenzene and 0.83 g. (4.0 mmol.) of rhodium trichloride, i.e. $RhCl_3$. The mixture was warmed to 100° C., carbon monoxide was bubbled through the mixture and 2.5 g. (16.0 mmol.) of 2,2,6,6,N-pentamethylpiperidine was added. Subsequent workup and analysis showed the presence of diphenylcarbonate (estimated yield 1%) and 0.7 g. (8%) of phenyl salicylate.

Examples VIII to XI

Preparation of phenylsalicylate using a preliminary reaction admixture, i.e. phenol, carbon monoxide and bis-(benzonitrile)palladium(II) dichloride and regulating relative to time the order of addition of a base, e.g. diisopropylmonoethylamine, to the preliminary reaction admixture.

A series of independent reactions were carried out wherein a preliminary reaction admixture, i.e. a "PRM", was contacted with a base, i.e. diisopropylmonoethylamine, 5, 20, 60 and 120 minutes after the PRM was initially contacted with carbon monoxide. A control run was carried out with base being added at zero minutes, e.g. essentially simultaneously with the formation of the PRM. Three hours after the combination of the PRM ingredients, the resulting reaction products were analyzed and the relative proportions of diphenylcarbonate and phenylsalicylate were determined. Summarized in Table I are the reaction parameters and products, i.e. the time of addition of the base to the PRM and the resulting reaction products, i.e. the diphenylcarbonate and the phenylsalicylate.

TABLE I

Example No.	Run No.	Base Addition Time (min)	Relative Proportions diphenylcarbonate:phenylsalicylate
Control	1.*	0	0.05 : 99.95
VIII	2.	5	0.25 : 99.75
IX	3.	20	5 : 95
X	4.	60	50 : 50
XI	5.	120	100 : 0

*-control run

As illustrated by this Example, the time and "order of addition" sequence, i.e. time and order of addition of base to a PRM in the practice of my process significantly effects the relative proportions and accordingly the yields of diphenyl-carbonate and phenylsalicylate obtained.

Example XII

Preparation of phenyl salicylate using palladium(II) dichloride as the Group VIIIB compound and copper(II)dichloride as the oxidant under carbon monoxide pressure.

A reaction vessel was charged with 94 g. (1.0 mole) of phenol, 34.0 g. (0.25 mol) of copper(II)dichloride, 0.45 g. (0.0025 mol) of palladium(II)dichloride, 147 g. (0.75 mol) of dicyclohexyl-N-methylamine, and 500 ml. of methylene chloride. The mixture was pressurized with 420 psig CO and heated to 160° C. for 4 hours, cooled and vented. Gas chromatography established the presence of 10.7 g. of phenyl salicylate (5% conversion based on phenol, 40% yield based on $CuCl_2$).

In the practice of the process, the Group VIIIB elements after separation from the resulting reaction products can be oxidized or reduced to any suitable oxidation state, and can be re-employed, that is, recycled in the aromatic salicylate process described herein.

WHAT WE CLAIM IS:-

1. A process for preparing an aromatic salicylate which comprises forming a mixture from a phenol, carbon monoxide, and a Group VIIIB element selected from ruthenium, rhodium, palladium, osmium, iridium or platinum having an oxidation state greater than zero, adding a base to the resulting mixture within a period of up to 120 minutes from formation of the mixture, and recovering at least a portion of said aromatic salicylate.
2. A process as claimed in claim 1, wherein said element is present in an ionic form.
3. A process as claimed in claim 1 or claim 2, wherein said element oxidation state is at least +2.
4. A process as claimed in any one of claims 1 to 3, wherein said base is a sterically hindered amine.
5. A process as claimed in any one of claims 1 to 4, wherein said element is associated with a carbonyl group.
6. A process as claimed in any one of claims 1 to 4, wherein said element is associated with a halide.
7. A process as claimed in any one of claims 1 to 4, wherein said element is coordinated with a ligand selected from a nitrile or a halide.
8. A process as claimed in any one of claims 1 to 4, wherein said element is associated with an inorganic halide compound.
9. A process as claimed in any one of the preceding claims wherein methylene chloride is employed as a solvent, the base is diisopropylmonoethylamine, the phenol is 4-methyl phenol, the Group VIIIB element is palladium in the form of palladium (II) dichloride.
10. A process as claimed in any one of claims 1 to 8, in which said salicylate is prepared in a methylene chloride solution in which the base is diisopropylmonoethylamine, the phenol is phenol, and the Group VIIIB element is palladium, in the form of bis(benzonitrile)-palladium (II) dichloride.
11. A process as claimed in any one of the preceding claims further comprising, after the preparation of the aromatic salicylate, separating at least a portion of any resulting Group VIIIB element or compound from said salicylate, oxidizing at least a portion of said resulting Group VIIIB element or compound to an oxidation state greater than zero, and recycling at least a portion of said oxidized element in said aromatic salicylate process.
12. A process as claimed in any one of the preceding claims carried out in the presence of a dehydrating agent.
13. A process as claimed in any one of the preceding claims carried out at a reaction

temperature of at least 150° C.

14. A process for making an aromatic salicylate substantially as hereinbefore described in any one of Examples 1 to XII.

15. An aromatic salicylate when produced by a process as claimed in any one of the preceding claims.

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