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(54) Preparation of 4-chlorobenzenesulfonyl chloride and 4,4′-dichlorodiphenyl sulfone

(57) A process for the preparation of 4-chlorobenzenesulfonyl chloride wherein chlorobenzene is reacted with chlorosulfonic acid in a halogenated aliphatic hydrocarbon in the presence of an alkali metal salt of a mineral acid and/or an ammonium salt of a mineral acid. After washing the resulting reaction mixture with water and separating the halogenated aliphatic hydrocarbon layer, water may be distilled off, together with the halogenated aliphatic hydrocarbon to obtain 4-chlorobenzenesulfonyl chloride in an anhydrous state. The 4-chlorobenzenesulfonyl chloride obtained can be converted into 4,4′-dichlorodiphenyl sulfone by reacting it with chlorobenzene in the presence of a catalytic amount of ferric chloride.

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SPECIFICATION

Improvements in or relating to the preparation of 4-chlorobenzenesulfonyl chloride and 4,4'-dichlorodiphenyl sulfone

This invention is concerned with improvements in or relating to the preparation of 4-chlorobenzenesulfonyl chloride and 4,4'-dichlorodiphenyl sulfone.

4-Chlorobenzenesulfonyl chloride is an important raw material for the preparation of 4,4'-dichlorodiphenyl sulfone which is a monomer used in the manufacture of polysulfone resins having excellent thermal resistance. Also, this substance is useful as a raw material for the manufacture of various drugs, agricultural chemicals, and dyes.

It is known that 4-chlorobenzenesulfonyl chloride can be prepared by reacting chlorobenzene with a stoichiometric excess of chlorosulfonic acid. For example, 4-chlorobenzenesulfonyl chloride has been prepared in a 72—73% yield by reacting 1 mole of chlorobenzene with 3 moles of chlorosulfonic acid, and it has been prepared in an 80% yield by using 8 moles of chlorosulfonic acid (A.M. Grigorovskiy et al., Zhur. Priklad, Khim., *28* 616—21(1955): Chem. Abstr., *50*, 3279(1956)). Moreover, the desired product has been prepared in a 70% yield by reacting 1 mole of chlorobenzene with 4 moles of chlorosulfonic acid at a temperature of 60°C (J.M. Dumont et al., Bull. Soc. Chim. France, *1962*, 1231—18; Chem Abstr., *57*, 9717(1962)). Thus, a large excess of chlorosulfonic acid is required to prepare 4-chlorobenzenesulfonyl chloride in an 80% or higher yield by the reaction of chlorobenzene with chlorosulfonic acid. Accordingly, if this method is put into industrial practice, there will be a great disadvantage from the viewpoint of economy and, in particular, environmental protection.

In the reaction of an aromatic compound with chlorosulfonic acid, an aromatic sulfonic acid and a diaryl sulfone are formed as by-products, along with the desired aromatic sulfonyl chloride. For example, when 1 mole of chlorobenzene is reacted with 3 moles of chlorosulfonic acid 4,4'-dichlorodiphenyl sulfone has been reported as a by-product in a 12% yield, along with 4-chlorobenzenesulfonyl chloride (61% yield) [F. Ullman et al., Ber., *40*, 641(1970)]. It is also stated in the aforementioned article by A. M. Grigorovskiy et al. that, when chlorosulfonic acid is used at a molar ratio of 3,4-chlorobenzenesulfonic acid (20% yield) and 4,4'-dichlorodiphenyl sulfone (8% yield) are formed as by-products. It is generally said that chloroform and carbon tetrachloride are useful for the purpose of suppressing side reactions in the reaction of an aromatic compound with chlorosulfonic acid [New Lectures on Experimental Chemistry, Vol. 14, "Syntheses and Reactions of Organic Compounds (III)", pp. 1787—1788, Maruzen (1978)]. When chlorobenzene is reacted with chlorosulfonic acid in such a solvent (for example, when 1 mole of chlorobenzene is reacted with 3 moles of chlorosulfonic acid in chloroform), no by-product worthy of mention is formed, but the yield of 4-chlorobenzenesulfonyl chloride is as low as 74.6% (Japanese Patent Publication No. 19457/'67).

In order to enhance the yield of 4-chlorobenzenesulfonyl chloride, there is a known method in which chlorosulfonic acid is reacted with sodium 4-chlorobenzenesulfonate. As described in the aforementioned article by Grigorovskiy et al., this method enables the desired product to be prepared in an 80% yield. It is also well known that this method can be carried out in an organic solvent. Specifically, there has been proposed a process in which 4-chlorobenzenesulfonyl chloride is prepared in a yield of as high as 89% by suspending dried sodium 4-chlorobenzenesulfonate in chloroform and then reacting it with chlorosulfonic acid in an amount of 2 moles per mole of the sodium 4-chlorobenzenesulfonate [M. Kulka, J. Am. Chem. Soc., *72*, 1215(1950)].

Although the amount of chlorosulfonic acid used is small and the yield is satisfactorily high, this process has the disadvantage that sodium 4-chlorobenzenesulfonate serving as one of the raw materials must be isolated and used in an anhydrous state. Thus, this process is not regarded as advantageous from an industrial point of view because it cannot be carried out economically.

Thus, it will be realized that there is a need for a process of reacting chlorobenzene with chlorosulfonic acid in which the amount of chlrorosulfonic acid used is minimized, the formation of by-products is suppressed, and 4-chlorobenzenesulfonyl chloride is obtained in high yield.

It is known that 4,4'-dichlorodiphenyl sulfone can be prepared by the Friedel-Crafts reaction in which 4-chlorobenzenesuflonyl chloride is reacted with chlorobenzene by using anhydrous ferric chloride as the catalyst (see, for example, U.S. Patent 3,334,146 (1967). In carrying out this process, however, the 4-chlorobenzenesulfonyl chloride is used in an anhydrous state.

As stated before, 4-chlorobenzenesulfonyl chloride can be prepared by reacting chlorobenzene with a stoichiometric excess of chlorosulfonic acid and this includes pouring the reaction mixture into ice water. In the process, 4,4'-dichlorodiphenyl sulfone is formed as a by-product. Accordingly, when the reaction mixture containing 4-chlorobenzenesulfonyl chloride and 4,4'-dichlorodiphenyl sulfone is poured into ice water and the resulting mixture is heated to 90°C, 4-chlorobenzenesulfonyl chloride is hydrolyzed to 4-chlorobenzenesulfonic acid. Accordingly, this process also serves to prepare 4,4'-dichlorodiphenyl sulfone when the 4-chlorobenzenesulfonic acid so formed is removed (U.S. Patent 2,860,168(1958)).

It can be seen that 4-chlorobenzenesulfonyl chloride is easily hydrolyzed to 4-chlorobenzenesulfonic acid. Accordingly, if it is desired to subject 4-chlorobenzenesulfonyl chloride obtained as above to the Friedel-Crafts reaction with chlorobenzene, it is dehydrated after completion of

the reaction to 4-chlorobenzenesulfonyl chloride, by e.g. pouring the reaction mixture into ice water, separating the product by filtration, and then drying it under reduced pressure.

Thus it will be realized that there is a need for a process of reacting chlorobenzene with chlorosulfonic acid in which anhydrous 4-chlorobenzenesulfonyl chloride is obtained in high yield.

Furthermore, a number of processes are known in which chlorobenzene used as a starting material is chlorosulfonylated and then converted into 4,4′-dichlorodiphenyl sulfone without isolating the intermediate product. They include, for example,

(1) a process in which chlorobenzene is reacted with sulfur trioxide to form 4-chlorobenzenesulfonic acid, a chlorinating agent or thionyl chloride is allowed to act thereon, and the 4-chlorobenzenesulfonyl chloride so formed is condensed with chlorobenzene (Japanese Patent Publication No. 5386/'81);

(2) a process in which chlorobenzene is reacted with both sulfur trioxide and thionyl chloride, and the 4-chlorobenzenesulfonyl chloride so formed is condensed with chlorobenzene [U.S.S.R. 568,637; Chem. Abstr., *87*, 167728 b(1977)]; and

(3) a process in which chlorobenzene is reacted with chlorosulfonic acid to form 4-chlorobenzenesulfonic acid, phosphorus oxychloride is reacted therewith, and the 4-chlorobenzenesulfonyl chloride so formed is condensed with chlorobenzene [U.S. Patent 3,125,604(1964)].

In these processes, inexpensive sulfonating agents such as sulfur trioxide and chlorosulfonic acid are used. However, the chlorinating agents used therein, i.e. thionyl chloride and phosphorus oxychloride, are relatively expensive and, therefore, the excess chlorinating agent is recovered after completion of the reaction. Accordingly, if these processes are put into industrial practice, there will be the disadvantages that provison for the recovery of the chlorinating agent must be made and the reuse of the recovered chlorinating agent is relatively difficult because it is easily decomposed. Thus, as methods for the industrial production of 4,4′-dichlorodiphenyl sulfone, none of the above-described processes are considered to be satisfactory from the viewpoint of either manufacturing convenience or economy.

4-Chlorobenzenesulfonyl chloride can be formed by reacting chlorobenzene with a stoichiometric amount of chlorosulfonic acid. However, if it is intended to form 4-chlorobenzenesulfonyl chloride according to this method and then subject it to the Friedel-Crafts reaction without isolating it, apart from questions of poor yield, consideration must be given to the amount of sulfuric acid formed as a by-product. More specifically, it is necessary to prepare anhydrous 4-chlorobenzenesulfonyl chloride by pouring the reaction mixture into ice water and passing the resulting mixture through filtering, water-washing and drying steps, and then subjecting this intermediate product to condensation reaction with chlorobenzene.

Nevertheless, using chlorobenzene and chlorosulfonic acid as the raw materials has the advantage that chlorosulfonic acid is easy to handle and industrially inexpensive; and it would be desirable to prepare 4,4′-dichlorodiphenyl sulfone by reacting chlorobenzene with chlorosulfonic acid to form 4-chlorobenzenesulfonyl chloride in an anhydrous state without isolating it, and then reacting it with chlorobenzene in the presence of ferric chloride.

It is an object of the present invention to provide an improved process for the preparation of 4-chlorobenzenesulfonyl chloride.

It is another object of the present invention to provide an improved process for the preparation of anhydrous 4-chlorobenzenesulfonyl chloride.

It is another object of the present invention to provide an improved process for the preparation of 4,4′-dichlorodiphenyl sulfone from chlorobenzene and chlorosulfonic acid *via* anhydrous 4-chlorobenzenesulfonyl chloride.

We have found that 4-chlorobenzenesulfonyl chloride can be prepared in high yield by reacting chlorobenzene with chlorosulfonic acid in a halogenated aliphatic hydrocarbon solvent in the presence of an alkali metal salt of a mineral acid and/or an ammonium salt of a mineral acid.

The invention provides a process for the preparation of 4-chlorobenzenesulfonyl chloride, wherein chlorobenzene is reacted with chlorosulfonic acid in an organic solvent comprising a halogenated aliphatic hydrocarbon and in the presence of a salt comprising an alkali metal salt of a mineral acid and/or an ammonium salt of a mineral acid.

Anhydrous 4-chlorobenzenesulfonyl chloride can be prepared by washing the reaction mixture with water, and then distilling off water, together with the solvent, from the separated organic solvent layer.

The invention also provides a process for the preparation of 4,4′-dichlorodiphenyl sulfone, wherein 4-chlorobenzenesulfonyl chloride prepared by a process as set out in the last preceding paragraph but one is reacted with chlorobenzene.

4,4′-Dichlorodiphenyl sulfone can be obtained by reacting anhydrous 4-chlorobenzenesulfonyl chloride with chlorobenzene in the presence of a catalytic amount of ferric chloride.

The invention also provides a process for the preparation of 4,4′-dichlorodiphenyl sulfone which comprises the steps of (a) reacting chlorobenzene with chlorosulfonic acid in the halogenated aliphatic hydrocarbon solvent in the presence of an alkali metal salt of a mineral acid and/or an ammonium salt of

a mineral acid; (b) washing the resulting reaction mixture with water, separating the organic solvent layer, and distilling off water, together with the organic solvent, to obtain 4-chlorobenzenesulfonyl chloride in an anhydrous state; and (c) reacting the resulting anhydrous 4-chlorobenzenesulfonyl chloride with chlorobenzene in the presence of a catalytic amount of ferric chloride.

The invention also provides 4-chlorbenzenesulfonyl chloride or 4,4'-dichlorodiphenyl sulfone when prepared by a process according to the invention.

There now follows a description of embodiments of the invention. This description, which is illustrative of process and product aspects of the invention, is given by way of example only, and not by way of limitation of the invention.

In a process embodying the present invention, reaction of chlorobenzene with chlorosulfonic acid is carried out in a halogenated aliphatic hydrocarbon solvent in the presence of an alkali metal salt of a mineral acid and/or an ammonium salt of a mineral acid.

The solvents which can be used are preferably halogenated lower aliphatic hydrocarbons of 1 or 2 carbon atoms which may have some or all of the hydrogen substituted by halogen. Examples of such halogenated aliphatic hydrocarbons include dichloromethane, chloroform, carbon tetrachloride, 1,1-dichloroethane, 1,2-dichloroethane, 1,1,1-trichloroethane, 1,1,2-trichloroethane, 1,1,1,2-tetrachloroethane, 1,1,2,2-tetrachloroethane, pentachloroethane, hexachloroethane, 1,2-dichloroethylene, trichloroethylene, tetrachloroethylene and analogous compounds obtained by replacing some or all of the chlorine with other halogens. The solvent is usually used in an amount of 0.5 to 5.0 times, preferably 1.0 to 3.0 times, the weight of the chlorobenzene.

Useful alkali metal salts of mineral acids include the halogenides, sulfates, sulfites, nitrates and phosphates of lithium, sodium and potassium. Useful ammonium salts of mineral acids include ammonium chloride, ammonium bromide, ammonium iodide, ammonium sulfate, ammonium sulfite, ammonium nitrate and ammonium phosphate. If desired, these alkali metal salts of mineral acids and ammonium salts of mineral acids may be used in combination. Such an alkali metal salt of a mineral acid and/or an ammonium salt of a mineral acid may be used in an amount of 0.01 to 5 moles, preferably 0.05 to 2 moles, per mole of the chlorobenzene. Although the alkali metal salt and/or ammonium salt may be used in an amount of more than 5 moles per mole of the chlorobenzene, a molar ratio of 5 or less generally suffices to produce satisfactory effects.

The results of using the solvent and the mineral acid salt(s) include for example the following: when 1 mole of chlorobenzene is reacted with 3 moles of chlorosulfonic acid at 55°—60°C, 4-chlorobenzenesulfonyl chloride is obtained in a 70% yield and 4,4'-dichlorodiphenyl sulfone is formed in a 9% yield. When the aforesaid reaction is carried out using 1,2-dichloroethane as the solvent, the desired product is obtained in a 69% yield and the corresponding sulfone is formed in a 10% yield: i.e. no significant difference in the yield of the desired product on the formation of by-products. Next, when 1 mole of chlorobenzene is reacted with 3 moles of chlorosulfonic acid at the aforesaid temperature in the presence of 0.3 mole of sodium chloride, the desired product is obtained in a 75% yield, and the amount of sulfone formed as a by-product is decreased. Although the addition of sodium chloride enhances the yield of the desired product only slightly, it is noteworthy that the formation of the sulfone by-product is suppressed. On the other hand, when 1 mole of chlorobenzene is reacted with 3 moles of chlorosulfonic acid at 55°—60°C in 1,2-dichloroethane in the presence of 0.3 mole of sodium chloride, the yield of the desired product is markedly increased to 90% and the yield of the by-product is as low as 2.5%. In addition to sodium chloride, alkali metal salts (e.g. lithium, sodium and potassium salts) and ammonium salts of mineral acids (e.g. hydrochloric acid, hydrobromic acid, hydroiodic acid, sulfuric acid, sulfurous acid, nitric acid, phosphoric acid) can also produce similar effects.

Thus, by reacting chlorobenzene with chlorosulfonic acid in a halogenated aliphatic hydrocarbon solvent in the presence of an alkali metal salt of a mineral acid and/or an ammonium salt of a mineral acid, it is possible to prepare the desired product in high yield while suppressing the formation of by-products.

The amounts of chlorobenzene and chlorosulfonic acid used are usually such that 2.5 to 4.0 moles, preferably 3.0 to 3.5 moles, of chlorosulfonic acid is provided for each mole of chlorobenzene. The reaction temperature generally ranges from 0° to 100°C, the preferred range being from 10° to 90°C.

Usually, the chlorobenzene is added dropwise to a mixture comprising the chlorosulfonic acid, the alkali metal salt and/or ammonium salt, and the organic solvent. Alternatively the chlorosulfonic acid may be added dropwise to a mixture comprising the chlorobenzene, the alkali metal salt and/or ammonium salt, and the organic solvent. After completion of the addition, the resulting reaction mixture is stirred at a predetermined temperature for a predetermined reaction time. Then, the reaction mixture is for example poured into ice water and the organic layer is separated. After the organic layer is washed with water and dried, the solvent is removed therefrom by distillation under reduced pressure to obtain the desired product, 4-chlorobenzenesulfonyl chloride.

In a preferred embodiment of the present invention, anhydrous 4-chlorobenzenesulfonyl chloride is obtained as follows: after completion of the reaction, the reaction mixture is usually cooled to room temperature and then washed with a sufficient amount of water to remove any by-product sulfuric acid and unreacted chlorosulonic acid that are present in the reaction mixture. More specifically, the reaction

mixture is usually washed by adding water thereto in an amount of for example, 5 to 6 times the weight of chlorosulfonic acid used. Thereafter, the organic solvent layer is separated. The solution so separated is heated under atmospheric pressure to distil off the water contained therein, as the aseotropic mixture with the solvent, and thereby obtain 4-chlorobenzenesulfonyl chloride in an anhydrous state.

Although 4-chlorobenzenesulfonyl chloride has the property of being easily hydrolyzed to 4-chlorobenzenesulfonic acid by heating it with water, the present process enables 4-chlorobenzenesulfonyl chloride to be readily prepared in an anhydrous state without hydrolysis problems; this is a quite unexpected and surprising fact in view of the prior art and the instability of 4-chlorobenzenesulfonyl chloride to water.

The anhydrous 4-chlorobenzenesulfonyl chloride prepared in the above described manner can be directly reacted with chlorobenzene in the presence of a catalytic amount of ferric chloride to produce 4,4′-dichlorodiphenyl sulfone. Specifically, chlorobenzene and ferric chloride are added to anhydrous 4-chlorobenzenesulfonyl chloride obtained as described above. The resulting reaction mixture is stirred at a predetermined temperature for a predetermined reaction time. After completion of the reaction, chlorobenzene is added to the reaction mixture so that its sulfone concentration may be adjusted to approximately 35 to 40%. After being cooled to a temperature of 65° to 70°C, the reaction mixture is washed with water at that temperature to remove the ferric chloride. Subsequently, the chlorobenzene is removed by steam distillation to obtain crystals of 4,4′-dichlorodiphenyl sulfone.

It will be noted that in the present process 4-chlorobenzenesulfonyl chloride is prepared in an anhydrous state and in high yield, and can be used directly, i.e. without being isolated, in the production of 4,4′-dichlorodiphenyl sulfone.

In the above-described preparation of 4,4′-dichlorodiphenyl sulfone by reacting anhydrous 4-chlorobenzenesulfonyl chloride with chlorobenzene in the presence of anhydrous ferric chloride, the amount of chlorobenzene used is for example in the range of 1.5 to 2.5 moles per mole of the 4-chlorobenzenesulfonyl chloride. The ferric chloride is usually used in an amount of 2 to 5 mole% based on the 4-chlorobenzenesulfonyl chloride, and greater amounts apparently produce no additional effect. The reaction temperature ranges from 140° to 160°C. The progress of the reaction can be readily followed by gas chromatography or high-speed liquid chromatography. Generally, the reaction is completed in 10 to 20 hours.

It will be realized that by the present process 4,4′-dichlorodiphenyl sulfone can be prepared from chlorobenzene and chlorosulfonic acid in high yield and without isolating the intermediate product.

The present invention is further illustrated by the following Examples.

EXAMPLE 1

In 250 g of 1,2-dichloroethane were suspended 349 g (3.0 moles) of chlorosulfonic acid and 17.5 g (0.3 mole) of sodium chloride. While this suspension was kept at a temperature of 55°—60°C, 112.5 g (1.0 mole) of chlorobenzene was added dropwise thereto over a period of 3 hours. The resulting reaction mixture was stirred at that temperature for an additional 5 hours, cooled to room temperature, and then poured into 1 liter of ice water. After this mixture was stirred well, the organic layer was separated therefrom. The same procedure was repeated by using 1 liter of ice water. After drying the separated organic layer, the solvent was removed therefrom by distillation under reduced pressure to obtain crystals of 4-chlorobenzenesulfonyl chloride. The results are shown in Table 1.

EXAMPLES 2 to 13

The desired product was obtained by repeating the procedure of Example 1, except that the amount of chlorosulfonic acid used, the type and amount of alkali metal salt of ammonium salt used, the type and amount of solvent used, and the reaction temperature were varied as indicated in Table 1. The results are shown in Table 1.

TABLE 1

Example No.	$ClSO_3H$ (moles)	Solvent	(g)	Alkali metal salt or ammonium salt	(mole)	Reaction temperature (°C)	Yield of 4-chlorobenzenesulfonyl chloride (% of theoretical)	Yield of 4,4'-dichlorodiphenyl sulfone (% of theoretical)
1	3.0	1,2-Dichloroethane	250	Sodium chloride	0.3	55—60	91.2	2.5
2	2.7	1,2-Dichloroethane	250	Sodium chloride	0.3	55—60	83.4	2.1
3	3.0	1,2-Dichloroethane	200	Potassium chloride	0.2	55—60	91.9	1.8
4	3.0	Chloroform	300	Lithium chloride	0.3	50—55	90.2	2.1
5	3.0	Carbon tetrachloride	350	Potassium bromide	0.2	50.55	91.0	2.4
6	3.0	1,1,2-trichloroethane	250	Potassium iodide	0.3	60—65	89.8	2.0
7	2.8	Carbon tetrachloride	315	Sodium sulfate	0.2	60—65	89.0	2.2
8	3.5	1,1,2-trichloroethane	200	Potassium nitrate	0.1	40—45	88.2	2.5
9	3.5	Trichloroethylene	175	Sodium phosphate	0.2	70—75	87.9	2.3
10	3.0	1,1,2,2-Tetrachloroethane	200	Sodium sulfite	0.1	65—70	87.0	2.3
11	4.0	1,2-Dichloroethane	215	Ammonium chloride	0.2	55—60	92.6	2.8
12	3.0	Tetrachloroethylene	175	Ammonium bromide	0.1	40—45	87.5	2.2
13	3.5	Tetrachloroethylene	150	Ammonium sulfate	0.08	25—30	84.0	2.6

EXAMPLE 14

In 250 g of 1,2-dichloroethane were suspended 349 g (3.0 moles) of chlorosulfonic acid and 17.5 g (0.3 mole) of sodium chloride. While this suspension was kept at a temperature of 55°—60°C, 112.5 g (1.0 mole) of chlorobenzene was added dropwise thereto over a period of 3 hours. The resulting reaction mixture was stirred at that temperature for an additional 5 hours and then cooled to room temperature. After the reaction mixture was washed by the addition of 1 liter of water, the organic layer was separated therefrom. The same procedure was repeated by using 1 liter of water. The separated solution was heated to distill off the solvent and thereby obtain crystals of 4-chlorobenzenesulfonyl chloride. The results are shown in Table 2.

EXAMPLES 15 to 26

The desired product was obtained by repeating the procedure of Example 14, except that the amount of chlorosulfonic acid used, the type and amount of alkali metal salt or ammonium salt used, the type and amount of solvent used, and the reaction temperature were varied as indicated in Table 2. The results are shown in Table 2.

TABLE 2

Example No.	$ClSO_3H$ (moles)	Solvent	(g)	Alkali metal salt or ammonium salt	(mole)	Reaction temperature (°C)	Yield of 4-chlorobenzenesulfonyl chloride (% of theoretical)	Yield of 4,4'-dichlorodiphenylsulfone (% of theoretical)	Water content (%)
14	3.0	1,2-Dichloroethane	250	Sodium chloride	0.3	55—60	91.3	2.5	0.01 or less
15	2.7	1,2-Dichloroethane	250	Sodium chloride	0.3	55—60	83.4	2.0	"
16	3.0	1,2-Dichloroethane	200	Potassium chloride	0.2	55—60	91.7	1.8	"
17	3.0	Chloroform	300	Lithium chloride	0.3	50—55	90.2	2.2	"
18	3.0	Carbon tetrachloride	350	Potassium bromide	0.2	50—55	91.0	2.4	"
19	3.0	1,1,2-trichloroethane	250	Potassium iodide	0.3	60—65	89.6	2.1	"
20	2.8	Carbon tetrachloride	315	Sodium sulfate	0.2	60—65	89.0	2.1	"
21	3.5	1,1,2-trichloroethane	200	Potassium nitrate	0.1	40—45	88.5	2.3	"
22	3.5	Trichloroethylene	175	Sodium phosphate	0.2	70—75	88.0	2.5	"
23	3.0	1,1,2,2-Tetrachloroethane	200	Sodium sulfite	0.1	65—70	87.3	2.4	"
24	4.0	1,2-Dichloroethane	215	Ammonium chloride	0.2	55—60	92.5	2.8	"
25	3.0	Tetrachloroethylene	175	Ammonium bromide	0.1	40—45	87.7	2.2	"
26	3.5	Tetrachloroethylene	150	Ammonium sulfate	0.08	25—30	84.1	2.5	"

EXAMPLE 27

In 250 g of 1,2-dichloroethane were suspended 349 g (3.0 moles) of chlorosulfonic acid and 17.5 g (0.3 mole) of sodium chloride. While this suspension was kept at a temperature of 55°—60°C, 112.5 g (1.0 mole) of chlorobenzene was added dropwise thereto over a period of 3 hours. The resulting reaction mixture was stirred at that temperature for an additional 5 hours and then cooled to room temperature. After the reaction mixture was washed by the addition of 1 liter of water, the organic layer was separated therefrom. The same procedure was repeated by using 1 liter of water. The separated solution was heated to distill off the solvent and thereby obtain crystals of 4-chlorobenzenesulfonyl chloride. To this product were added 214 g (1.9 moles) of chlorobenzene and 3.1 g of ferric chloride. While being kept at 145°—155°C, this reaction mixture was stirred for 15 hours. After the addition of 250 g of chlorobenzene, the resulting mixture was cooled to 70°C and washed at that temperature by the addition of 1 liter of water. After the organic layer was separated, chlorobenzene was removed therefrom by steam distillation to obtain crystals of 4,4′-dichlorodiphenyl sulfone. The results are shown in Table 3.

EXAMPLES 28 to 39

The desired product was obtained by repeating the procedure of Example 27, except that the amount of chlorosulonic acid used, the type and amount of alkali metal salt or ammonium salt used, the type and amount of solvent used, and the reaction temperature were varied as indicated in Table 3. The results are shown in Table 3.

TABLE 3

Example No.	Preparation of 4-chlorobenzenesulfonyl chloride						Preparation of 4,4'-dichloro-diphenyl sulfone	
	$ClSO_3H$ (moles)	Solvent	(g)	Alkali metal salt or ammonium salt	(mole)	Reaction temperature (°C)	Yield (%)	Purity (%)
27	3.0	1,2-Dichloro-ethane	250	Sodium chloride	0.3	55—60	93.2	89.5
28	2.7	1,2-Dichloro-ethane	250	Sodium chloride	0.3	55—60	87.9	88.5
29	3.0	1,2-Dichloro-ethane	200	Potassium chloride	0.2	55—60	93.6	89.2
30	3.0	Chloroform	300	Lithium chloride	0.3	50—55	92.4	88.7
31	3.0	Carbon tetra-chloride	350	Potassium bromide	0.2	50—55	91.7	88.4
32	3.0	1,1,2-trichloro-ethane	250	Potassium iodide	0.3	60—65	90.5	88.4
33	2.8	Carbon tetra-chloride	315	Sodium sulfate	0.2	60—65	90.2	89.0
34	3.5	1,1,2-trichloro-ethane	200	Potassium nitrate	0.1	40—45	89.5	89.1
35	3.5	Trichloro-ethylene	175	Sodium phosphate	0.2	70—75	89.3	89.0
36	3.0	1,1,2,2-Tetra-chloroethane	200	Sodium sulfite	0.1	65—70	88.5	88.8
37	4.0	1,2-Dichloro-ethane	215	Ammonium chloride	0.2	55—60	93.8	89.8
38	3.0	Tetrachloro-ethylene	175	Ammonium bromide	0.1	40—45	89.7	88.0
39	3.5	Tetrachloro-ethylene	150	Ammonium sulfate	0.08	25—30	87.9	89.1

CLAIMS

1. A process for the preparation of 4-chlorobenzenesulfonyl chloride, wherein chlorobenzene is reacted with chlorosulfonic acid in an organic solvent comprising a halogenated aliphatic hydrocarbon and in the presence of a salt comprising an alkali metal salt of a mineral acid and/or an ammonium salt of a mineral acid.

2. A process according to claim 1, wherein the chlorosulfonic acid is used in an amount of 2.5 to 4.0 moles per mole of the chlorobenzene.

3. A process according to claim 1, wherein the chlorosulfonic acid is used in an amount of 3.0 to 3.5 moles per mole of the chlorobenzene.

4. A process according to any one of claims 1, 2 and 3, wherein the reaction is carried out at a temperature of 0° to 100°C.

5. A process according to any one of claims 1, 2 and 3, wherein the reaction is carried out at a temperature of 10° to 90°C.

6. A process according to any one of the preceding claims, wherein the halogenated aliphatic hydrocarbon has one or two carbon atoms.

7. A process according to any one of the preceding claims, wherein the halogenated aliphatic hydrocarbon is used in an amount of 0.5 to 5.0 times the weight of the chlorobenzene.

8. A process according to any one of claims 1 to 6, wherein the halogenated aliphatic hydrocarbon is used in an amount of 1.0 to 3.0 times the weight of the chlorobenzene.

9. A process according to any one of the preceding claims, wherein the salt comprises a halogenide, sulfate, sulfite, nitrate or phosphate of lithium, sodium, potassium or ammonium.

10. A process according to any one of the preceding claims, wherein the alkali metal or ammonium salt is used in an amount of 0.01 to 5 moles per mole of the chlorobenzene.

11. A process according to any one of the preceding claims, wherein the reaction is carried out by adding the chlorobenzene dropwise to a mixture of the chlorosulfonic acid, the salt and the organic solvent.

12. A process according to any one of the preceding claims, wherein the reaction mixture is washed with water and the water distilled off, together with the organic solvent to obtain 4-chlorobenzenesulfonyl chloride in an anhydrous state.

13. A process according to claim 12, wherein the amount of water used in washing the reaction mixture is sufficient to remove any by-product sulfuric acid or unreacted chlorosulfonic acid that are present in the reaction mixture.

14. A process according to claim 12 or claim 13, wherein the washing is carried out by adding water to the reaction mixture in an amount of 5 to 6 times the weight of chlorosulfonic acid used and then stirring the resulting mixture.

15. A process according to any one of claims 12, 13 and 14, wherein the washing is carried out at room temperature.

16. A process for the preparation of 4-chlorobenzenesulfonyl chloride substantially as hereinbefore described with reference to any one of the Examples.

17. A process for the preparation of 4,4′-dichlorodiphenyl sulfone, wherein 4-chlorobenzenesulfonyl chloride prepared by a process according to any one of the preceding claims is reacted with chlorobenzene.

18. A process for the preparation of 4,4′-dichlorodiphenyl sulfone which comprises the steps of

(a) reacting chlorobenzene with chlorosulfonic acid in a halogenated aliphatic hydrocarbon solvent in the presence of an alkali metal salt of a mineral acid and/or an ammonium salt of a mineral acid;

(b) washing the resulting reaction mixture with water, separating the organic solvent layer, and distilling off water, together with the organic solvent, to obtain 4-chlorobenzenesulfonyl chloride in an anhydrous state; and

(c) reacting the resulting anhydrous 4-chlorobenzenesulfonyl chloride with chlorobenzene in the presence of a catalytic amount of ferric chloride.

19. A process for the preparation of 4,4′-dichlorodiphenyl sulfone substantially as hereinbefore described with reference to any one of Examples 27 to 39.

20. 4-Chlorobenzenesulfonyl chloride when prepared by a process according to any one of claims 1 to 16.

21. 4,4′-Dichlorodiphenylsulfone when prepared by a process according to any one of claims 17, 18 and 19.

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