

Preparation of α -chloroisopropyl-substituted aromatics

The present invention relates to a process for preparing
5 α -chloroisopropyl-substituted aromatics.

α -Chloroisopropyl-substituted aromatics, such as m- or p-dicumyl chloride or 1,3,5-tricumyl chloride, served as inifer molecules for preparing linear or star-shaped telechelic polyisobutenes.

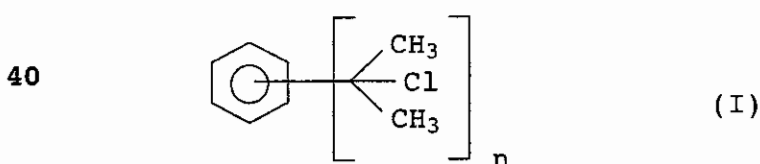
10 The reaction of the inifer with a Lewis acid results in a complex having 2 or 3 carbocationic or cationogenic centers which can add onto isobutene molecules. The carbocationic tert-butyl termini of the linear or star-shaped polyisobutenes obtained may be converted to olefinic or other functional groups, cf., for
15 example, EP-A 0 713 883.

J.P. Kennedy, L.R. Ross, J.E. Lackey, O. Nuyken, Polym. Bull. 1981, 4, 67-74 describe the synthesis of 1,3,5-tris(α -chloroisopropylbenzene) by reacting
20 1,3,5-triisopropenylbenzene with hydrogen chloride in dichloromethane at 0°C. For the workup, the dichloromethane has to be distilled off.

On the other hand, O. Nuyken, G. Maier, D. Young, M.B. Leitner, 25 Macromol. Chem., Macromol. Symp. 60, (1992) 57-63 disclose that 1,4-diisopropenylbenzene forms a polymer having 1,1,3-trimethylindane or α -methylstyrene repeating units under the influence of Lewis or Brönsted acids.

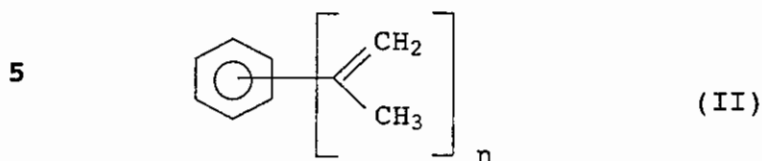
30 It is an object of the present invention to provide a process by which α -chloroisopropyl-substituted aromatics is obtained in high yield and with simple workups.

We have found that this object is achieved by a process for
35 preparing α -chloroisopropyl-substituted aromatics of the formula
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where n is an integer from 2 to 4

by treating isopropenyl-substituted aromatics of the formula II



10 with hydrogen chloride in the absence of a solvent.

- The process according to the invention allows α -chloroisopropyl-substituted aromatics to be obtained in virtually quantitative yields. This is surprising to a high
- 15 degree, since those skilled in the art would have expected a reaction in the absence of a solvent to result in the occurrence of numerous undesired secondary reactions or the cationic polymerization of the isopropenyl-substituted aromatics (cf. O. Nuyken et al., loc. cit.). The success of the process according
- 20 to the invention is believed to be based on the instability of carbocations, from which undesired secondary reactions or polymerizations can start, in the absence of a solvent, in particular of a polar solvent.
- 25 The process according to the invention can be carried out in a simple manner by passing hydrogen chloride gas through the isopropenyl-substituted aromatics or by reacting it therewith in a pressure vessel. This utilizes the fact that both the reactant and the product of the process according to the invention are
- 30 liquid at reaction temperature and that the use of a solvent is unnecessary. The workup is generally limited to the removal of excess hydrogen chloride gas from the product, for example by stripping with inert gas such as nitrogen. Yield losses resulting from workup steps are avoided.
- 35 The process according to the invention is preferably effected at a temperature of from -10 to $+50^{\circ}\text{C}$, in particular from 0 to 15°C , and a pressure from 1 to 10 bar. It may be carried out batchwise or continuously.
- 40 The reaction may optionally be accelerated by using Lewis or Brönsted acid catalysts. Useful catalysts include Lewis acids such as aluminum trichloride, aluminum tribromide, boron trifluoride, boron trifluoride alkoxide, boron trifluoride
- 45 etherate, titanium tetrachloride, tin tetrachloride, ethylaluminum dichloride, iron trichloride, antimony pentachloride or antimony pentafluoride; Brönsted acids such as

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sulfuric acid, phosphoric acid, trifluoromethanesulfonic acid and the like. Organic protic acids may also be present in polymerically bound form, for example as ion exchanger resins.

- 5 In the formulae I and II, n is preferably 2 or 3. Preferred isopropenyl-substituted aromatics are 1,3,5-triisopropenylbenzene, 1,4-diisopropenylbenzene and 1,3-diisopropenylbenzene, and particular preference is given to the latter. Apart from the isopropenyl substituents, the benzene
- 10 ring may bear further substituents which do not impair the reaction according to the invention, in particular C₁-C₄-alkyl radicals such as methyl, ethyl or t-butyl. Useful reactants for the process according to the invention also include mixtures of different isopropenyl-substituted aromatic.
- 15 The isopropenyl-substituted aromatics used as reactants are known and obtainable, for example, by dehydrating α -hydroxyl-substituted aromatics (cf. DE-A 1 618 449), Wittig reaction of acetylbenzenes (cf. J.P. Kennedy et al., Polym. Bull. 20 1981, 4, 67-74) or by dehydrogenating isopropylbenzenes (cf. JP-2001026558 and JP-2000327596).

- The α -chloroisopropyl-substituted aromatics obtained by the process according to the invention can be used in a manner known
- 25 per se for preparing homopolymers of isobutene or copolymers of isobutene with vinylaromatics by living cationic polymerization. On this subject, reference is made, for example, to EP-A 0 713 883, DE-A 199 37 562 or DE-A 100 61 715.

- 30 The invention is illustrated by the examples which follow.

Example 1:

- A 1 l four-necked flask was initially charged with 500 g
- 35 (3.16 mol) of 1,3-diisopropenylbenzene. 290 g (7.95 mol) of hydrogen chloride were passed in within 7.5 h with cooling to an internal temperature of 5°C and at atmospheric pressure. Unconverted HCl was then removed by stripping with nitrogen. 715 g (98%) of 1,3-bis(α -chloroisopropyl)benzene remained as a
- 40 colorless liquid; chlorine content 29.3%; ¹H-NMR (CD₂Cl₂, 360 MHz): 2.00 (s, 12 H, methyl), 7.29-7.52 (m, 3 H, aromat. H), 7.82-7.83 (m, 1 H, aromat. H).

Example 2:

- 45 A 500 ml four-necked flask was initially charged with 200 g (1.26 mol) of 1,3-diisopropenylbenzene. 135 g (3.70 mol) of

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hydrogen chloride were passed in within 8 h with cooling to an internal temperature of 5°C and at atmospheric pressure.

Unconverted HCl was then removed under reduced pressure. 288 g (99%) of 1,3-bis(α -chloroisopropyl)benzene remained as a

- 5 colorless liquid; chlorine content 28.6%; $^1\text{H-NMR}$ (CD_2Cl_2 , 360 MHz): 2.00 (s, 12 H, methyl), 7.29-7.52 (m, 3 H, aromat. H), 7.82-7.83 (m, 1 H, aromat. H).

Comparative Example 3:

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A 2 l four-necked flask was initially charged with 200 g (1.26 mol) of 1,3-diisopropenylbenzene in 750 ml of CH_2Cl_2 and this was then admixed with about 1 ml of ethanol. 12.5 g (3.42 mol) of hydrogen chloride were passed in within 7 h with cooling

- 15 to an internal temperature of 5°C and at atmospheric pressure. The solvent and also unconverted HCl was then removed under reduced pressure. 264 g (90%) of 1,3-bis(α -chloroisopropyl)benzene remained as a colorless liquid; chlorine content 29.2%; $^1\text{H-NMR}$ (CD_2Cl_2 , 360 MHz): 2.00 (s, 12 H, methyl), 7.29-7.52 (m, 3 H, aromat. H), 7.82-7.83 (m, 1 H, aromat. H).

Example 4:

An autoclave was initially charged with 490 g (3.10 mol) of

- 25 1,3-diisopropenylbenzene. 200 g (5.6 mol) of HCl were metered in within 3 h in such a manner that the internal pressure was 5 bar and the internal temperature did not exceed 30°C. The remaining HCl was removed by stripping with nitrogen. 705 g (99%) of 1,3-bis(α -chloroisopropyl)benzene were obtained as a colorless
- 30 liquid; chlorine content 30.6%; $^1\text{H-NMR}$ (CD_2Cl_2 , 360 MHz): 2.00 (s, 12 H, methyl), 7.29-7.52 (m, 3 H, aromat. H), 7.82-7.83 (m, 1 H, aromat. H).

Example 5:

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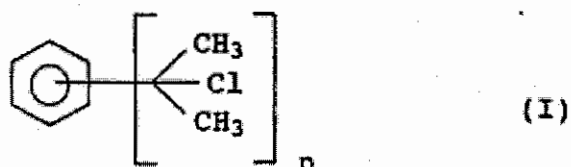
A 40 l V4A steel stirred reactor was initially charged with 18.0 kg (114 mol) of 1,3-diisopropenylbenzene. 10.1 kg (277 mol) of hydrogen chloride were passed in within 8 h at an internal temperature of 5-10°C (brine cooling) and an internal pressure of

40 1.1 bar. The remaining HCl was removed by stripping with nitrogen. 26 kg (99%) of 1,3-bis(α -chloroisopropyl)benzene were obtained as a colorless liquid; chlorine content 30.1%; $^1\text{H-NMR}$ (CD_2Cl_2 , 360 MHz): 2.00 (s, 12 H, methyl), 7.29-7.52 (m, 3 H, aromat. H), 7.82-7.83 (m, 1 H, aromat. H).

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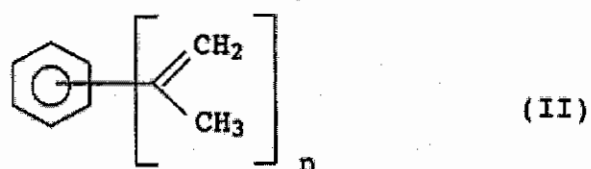
We claim:

1. A process for preparing α -chloroisopropyl-substituted aromatics of the formula I



where n is an integer from 2 to 4

by treating isopropenyl-substituted aromatics of the formula II



with hydrogen chloride in the absence of a solvent.

2. A process as claimed in claim 1, wherein the treatment is effected at a temperature of from -10 to 50°C.
3. A process as claimed in claim 1 or 2, wherein the treatment is effected at a pressure of from 1 to 10 bar.
4. A process as claimed in any of the preceding claims, wherein 1,3-diisopropenylbenzene is used as iso-propenyl-substituted aromatic of the formula II.