(12) UK Patent Application (19) GB (11) 2 087 377 A

(21) Application No **8037167**
(22) Date of filing
19 Nov 1980
(43) Application published
26 May 1982
(51) **INT CL³ C07C 17/14**
(52) Domestic classification
C2C 220 227 22Y 313 31Y 338 339 440 441 444 564 56Y 776 EJ FB HF
(56) Documents cited
None
(58) Field of search
C2C
(71) Applicant
Dow Chemical Company Limited
Meadowbank
Bath Road
Hounslow
Middlesex TW5 9QY
(72) Inventors
David Philip Clifford
Robert Arthur Sewell
(74) Agents
Boult Wade & Tennant
27 Furnival Street
London EC4A 1PQ
United Kingdom

(54) **Preparation of 2-chlorobenzotrichloride**

(57) High yields of 2-chlorobenzotrichloride are obtained by reacting 2-chlorotoluene with chlorine in the presence of phosphorus pentachloride.

GB 2 087 377 A

SPECIFICATION

Preparation of 2-chlorobenzotrichloride

This invention relates to a process for making 2-chlorobenzotrichloride by reacting 2-chlorotoluene with chlorine in the presence of phosphorus pentachloride.

The reaction of 2-chlorotoluene with chlorine in the presence of actinic light or phosphorus tri-chloride and heat is known. See, for example, Proc. Inst. Przem. Org. 1973 *5* pp. 9–23. Reaction times of 5.5 to 24 hours are disclosed and the yield of the desired 2-chlorobenzotrichloride is in the range of 6 to 16 percent.

We have now found that the reaction of 2-chlorotoluene with chlorine proceeds readily to 2-chlorobenzotrichloride when one employs phosphorus pentachloride as catalyst and reaction temperatures of 150° to 260°C, preferably temperatures of 190° to 255°C.

By the process of this invention, yields of 85 to 95 percent are readily obtained and the production of undesired by-products is considerably reduced.

Chlorine is advantageously present in at least a slight excess, and is preferably present in a substantial excess in order to obtain faster reaction rates and higher yields.

Phosphorus pentachloride may be employed in an amount of from 0.1 to 25 weight percent, based on the 2-chlorotoluene, but is advantageously present in an amount of from 0.5 to 2 weight percent.

This invention is further illustrated by the following examples.

Example 1

2-Chlorotoluene (253 g, 2 moles) and PCl_5 (2.5 g) were heated to 190°C, chlorine was introduced via a gas sparge tube at a rate slightly greater than its uptake. After 10 hours the mixture was cooled, made up to known volume in carbon tetrachloride and assayed by gas chromatography (GC) against an external standard. Yield 94 percent.

Example 2

Repeat of Example 1 at 150°C. After 29 hours the reaction was assayed. Yield 14 percent against external standard. Substantial amount of intermediates were observed.

Example 3

2-Chlorotoluene (63.25 g, 0.5 mole) and PCl_5 (0.625 g) were heated to 190°C. Chlorine was introduced via a gas sparge tube at a rate much greater than its uptake. After 8.5 hours the mixture was cooled, distilled and the distillate made up to known volume in carbon tetrachloride and assayed by GC against an external standard. Yield 93 percent (95 percent when corrected for 2-chlorotoluene purity of 98 percent).

Example 4

2-Chlorotoluene (63.25 g, 0.5 mole) and PCl_5 (0.625 g) were heated at reflux for four hours. Chlorine was introduced via a gas sparge tube at a rate much greater than its uptake. Reflux began at 160°C, rising to 254°C at the completion of the reaction. The reaction mixture was cooled and a small portion was made up to known volume in carbon tetrachloride and assayed by GC against an external standard. Yield 87 percent. The remainder of the reaction mixture was distilled and the distillate made up to known volume in carbon tetrachloride and assayed by GC against an external standard. Yield 87 percent.

Example 5

A repeat of Example 4 with no PCl_5 present gave, after 4.5 hours, a yield of only 68 percent (assayed by GC against an external standard). After distillation a dark brown polymeric residue weighing 22 grams remained.

Example 6

Example 4 was again repeated employing 6.3 g (10 weight percent) of PCl_5. After 4 hours the reaction assayed 86 percent yield. A polymeric residue of 7 g remained after distillation.

Example 7

2-Chlorotoluene (63.25 g, 0.5 mole) and PCl_5 (0.625 g) were heated to 175°C. Chlorine was introduced via a gas sparge tube at a rate slightly greater than its uptake. After 17.5 hours the mixture was cooled, made up to known volume in carbon tetrachloride and assayed by GC against an external standard. Yield 42 percent. No starting material or intermediates remained. GC showed substantial amounts of a slower running impurity. Analysis by microwave plasma detection gave the empirical formula as $C_7H_3Cl_5$, i.e. ring chlorination had taken place.

CLAIMS

1. A process for the preparation of 2-chlorobenzotrichloride which process comprises reacting 2-chlorotoluene with chlorine in the presence of phosphorus pentachloride at a temperature in the range of from 150°to 260°C.

2. A process as claimed in claim 1 wherein the temperature is in the range of from 190° to 225°C.

3. A process as claimed in claim 1 or claim 2 wherein the chlorine is present in a substantial excess throughout the course of reaction.

4. A process as claimed in claim 2 or claim 3 wherein the reaction is completed in 10 hours or less.

5. A process as claimed in any one of the

preceding claims wherein the phosphorus pentachloride is employed in an amount of from 0.1 to 25 weight percent, based on the 2-chloro-toluene.

6. A process for preparing 2-chlorobenzotrichloride as claimed in claim 1 substantially as hereinbefore described with reference to any one of Examples 1 to 4, 6 or 7.

7. 2-Chlorobenzotrichloride whenever prepared by a process as claimed in any one of the preceding claims.

Printed for Her Majesty's Stationery Office
by Burgess & Son (Abingdon) Ltd.—1982.
Published at The Patent Office. 25 Southampton Buildings
London, WC2A 1AY, from which copies may be obtained.