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Chlorination of bis- and Chloro-bis-(perfluoroalkyl)-benzenes[1]

BY EARL T. MCBEE AND MARVIN R. FREDERICK[1a]

Chloro derivatives of trifluoromethylbenzene have been prepared[2] by chlorinating the latter in liquid phase at atmospheric pressure in the presence of iron(III) chloride. However, this procedure is not applicable to the chlorination of 1,3- and 1,4-bis-(trifluoromethyl)-benzenes[3] and similar compounds of longer side-chains since these compounds are more difficultly substituted. Chloro-bis-(trifluoromethyl)-benzenes have been prepared by fluorination of the chloro-bis-(trichloromethyl)-benzenes.[4,5] Since this paper was first submitted for publication, the chlorination of bis-(trifluoromethyl)-benzenes in an iron reactor at 150–170° under a chlorine pressure of 300 pounds per square inch has been described.[6]

A procedure generally applicable to the preparation of chloro-bis-(perfluoroalkyl)-benzenes has been devised which comprises vapor-phase chlorination at atmospheric pressure of a bis (perfluoroalkyl)-benzene in contact with activated carbon impregnated with an inorganic chloride. Iron(III) chloride was found to be the most satisfactory of the inorganic chlorides studied. No appreciable amount of the iron(III) chloride sublimed from the reactor and the catalyst showed little decrease in activity with use. Antimony(V) chloride was less effective than iron(III) chloride for chlorinations at temperatures below 250°. However, higher percentages of polychlorinated compounds were found in the product when the antimony catalyst was used. Antimony(V) chloride distilled from the reactor and, as a consequence, there was a rapid decline in catalyst activity. Nickel chloride on activated carbon was of about the same activity as iron(III) chloride. Iron, iron(III) chloride, or activated carbon used alone were much less active than activated carbon impregnated with an inorganic chloride.

Hydrolysis of the chloro derivatives of bis-(perfluoroalkyl)-benzenes by 60–80% sulfuric acid to the corresponding terephthalic and isophthalic acids[7] was used to establish structures.

Experimental

Preparation of Starting Materials

bis-(Perfluoroalkyl)-benzenes.—The bis-(trifluoromethyl)-benzenes were made from the corresponding bis-(trichloromethyl)-benzene by fluorination with anhydrous hydrogen fluoride in the presence of antimony(V) chloride at room temperature.[5] The bis-(pentafluoroethyl)-benzenes[8] and 1-(pentafluoroethyl)-4-(trifluoromethyl)-benzene[9] were prepared as described previously.

Catalysts.—The activated carbon-iron(III) chloride catalyst was prepared by soaking 200 g. of Columbia grade 8G, 8/14 mesh activated carbon in a solution of 60 g. of iron(III) chloride in 200 ml. of water made slightly acidic with hydrochloric acid. After soaking for one hour, the carbon was heated, first to 200°, and finally for twelve hours at 300°. The activated carbon–antimony(V) chloride catalyst was prepared by pouring antimony(V) chloride over activated carbon and then heating to 300°.

Chlorinations

Apparatus and Technique.—A 3-liter, 3-necked flask equipped with a chlorine inlet, a thermometer, a reactor constructed either of glass or nickel 20 mm. by 500 mm., and a liquid return was used for the chlorinations. Chlorine was introduced through a flowmeter above the surface of the liquid in the flask. The reaction temperature was measured by a thermocouple or thermometer placed in the center of the reactor. Vapors issuing from the reactor passed through a water-cooled condenser welded directly to the reactor. Liquids were returned to the flask through a liquid trap and the gases were vented to an appropriate scrubber.

The technique used is illustrated by the following example. bis-(Trifluoromethyl)-benzenes (1263 g., 5.9 moles) prepared from technical xylene were poured into the flask. The reactor, packed with a catalyst of active carbon and iron(III) chloride, was heated to 250°, the material in the flask was heated to reflux (114°), and chlorine was added at about 0.8 mole per hour. Chlorination was continued for thirty-one hours, at the end of which time the boiling point of the contents of the flask was 127°. The product was removed from the flask, washed with a sodium bicarbonate solution, and then with water, dried, and rectified. There was obtained 438 g. (2.10 mole) of unreacted bis-(trifluoromethyl)-benzenes, 476 g. (1.91 moles) of chloro-bis-(trifluoromethyl)-benzenes composed of 5-chloro-1,3-bis-(trifluoromethyl)-benzene (b. p. 137–137.5°) and 2-chloro-1,4-bis-(trifluoromethyl)-benzene (b. p. 147–148°), and 486 g. (1.72 moles) of dichloro-bis-(trifluoromethyl)-benzenes. Conversions to chloro- and dichloro-bis-(trifluoromethyl)-benzenes were 32% and 29%, respectively. The yield of chloro-bis-(trifluoromethyl)-benzenes was 97%.

1,4-bis-(Trifluoromethyl)-benzene, 2-chloro-1,4-bis-(trifluoromethyl)-benzene, 1,3-bis-(trifluoromethyl)-benzene, 1-(pentafluoroethyl)-4-(trifluoromethyl)-benzene and bis-(pentafluoroethyl)-benzenes were chlorinated in a similar manner at temperatures in the range 200–250°. Properties of the chloro-bis-(perfluoroalkyl)-benzenes obtained are summarized in Table I.

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(2) L. C. Holt and H. Wilkens, U. S. Patents 2,174,512 (Oct. 3, 1939) and 2,174,513 (Oct. 3, 1939).

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(7) E. Wertyporoch, *Ann.*, **493**, 1536-1565 (1932).

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TABLE I

CHLORO-(PERFLUOROALKYL)-BENZENES

					Analyses, %					
					Obs.			Calcd.		
Compound	B. p., °C. 748 mm.	M. p., °C.	$n^{25}\text{D}$	d^{25}_4	Cl	F	Mol. wt.	Cl	F	Mol. wt.
bis-(Trifluoromethyl)-benzenes										
5-Chloro-1,3-	137.3–137.5	−22.2 to −22.0	1.4043	1.484	14.1	45.6	245	14.3	45.7	248.5
Dichloro-1,3-[a]	173.0–173.2	−36 to −35	1.4372	1.609	25.0	40.9	281	25.1	40.4	283
Trichloro-1,3-[a]	209.2–209.4	−2 to −1	1.4704	1.713	33.2	36.0	319	33.6	36.0	317.5
2,3,5-Trichloro-1,4-	209.6–209.8	−12 to −11	1.4711	1.711	33.4	35.8	314	33.6	36.0	317.5
2,5-Dichloro-1,4-	174.4–174.6	34.6 to 34.9	....	...	25.1	40.9	286	25.1	40.4	283
Tetrachloro-1,4-	245.5–245.8	48.3 to 48.6	....	...	40.6	31.9	350	40.4	32.4	352
1-(Pentafluoroethyl)-4-(trifluoromethyl)-benzenes										
2,5-Dichloro-	180.9–181.0	Sets to glass	1.4250	1.648	21.4	46.0	332	21.6	45.6	333
Trichloro-[a]	213.8–214.0	....	....	...	29.3	41.7	366	29.0	41.4	367.5
Tetrachloro-	247.6–248	50.4 to 51.2	....	...	33.6	37.9	403	35.4	37.8	402
bis-(Pentafluoroethyl)-benzenes										
5-Chloro-1,3-	153.3–153.6	−22.5 to −22.0	1.3791	1.568	9.9	..	346	10.2	54.7	348.5
2-Chloro-1,4-	164.8–164.9	−21.0 to −20.5	1.3871	1.601	10.0	..	349	10.2	54.7	348.5
2,5-Dichloro-1,4-	187.8–188.1	39.0 to 39.5	....	...	18.9	50.0	320	18.6	49.6	383
Tetrachloro-1,4-	250.0–252.4	97.5 to 98.3	....	...	31.2	42.4	445	31.4	42.0	452

[a] These materials are probably mixtures.

Summary

A procedure generally applicable to the preparation of chloro-bis-(perfluoroalkyl)-benzenes has been devised which involves vapor-phase chlorination of a bis-(perfluoroalkyl)-benzene in contact with activated carbon catalyst impregnated with an inorganic chloride. Iron(III) chloride was found to be the most satisfactory of the catalysts studied.

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[10] Original manuscript received November 28, 1947.

NOTES

Concerning the Structure of D-Glucosone

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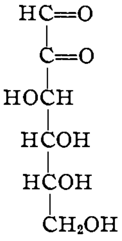
The structure of D-glucosone has not been definitely established.

Since it reacted in the cold with various hydrazines, particularly methyl phenylhydrazine, Fischer[2] believed that D-glucosone existed as the keto-aldehyde, I.

Since it reacted with Schiff reagent in the cold and was bound by sodium sulfite, Dixon and Harrison[3] concluded that D-glucosone contained a free carbonyl group.

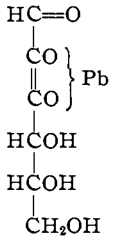
Because of the selective absorption shown by its aqueous solutions in ultraviolet light, Bednarczyk and Marchlewski[4] felt that D-glucosone, like D-fructose and D-sorbose, possessed a free carbonyl group.

Evans, *et al.*,[5] have speculated that Fischer's lead–glucosone complex might be the salt of a 2,3-enediol



$$\begin{array}{c} \mathrm{HC{=}O} \\ | \\ \mathrm{C{=}O} \\ | \\ \mathrm{HOCH} \\ | \\ \mathrm{HCOH} \\ | \\ \mathrm{HCOH} \\ | \\ \mathrm{CH_2OH} \end{array}$$

I



$$\begin{array}{c} \mathrm{HC{=}O} \\ | \\ \left.\begin{array}{c}\mathrm{CO} \\ \| \\ \mathrm{CO}\end{array}\right\}\mathrm{Pb} \\ | \\ \mathrm{HCOH} \\ | \\ \mathrm{HCOH} \\ | \\ \mathrm{CH_2OH} \end{array}$$

II

Hynd[6] retained Fischer's formula for D-glucosone but considered it possible that the compound might later be proved to contain one, or perhaps two, oxidic rings.

Since, in his opinion, the osones showed none of the characteristic reactions of the aldehydes

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[1] Taken in part from a thesis submitted by Charles E. Becker to the Faculty of the Graduate School in partial fulfillment of the requirements for the degree Master of Arts in the Department of Chemistry, Indiana University, 1948.

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