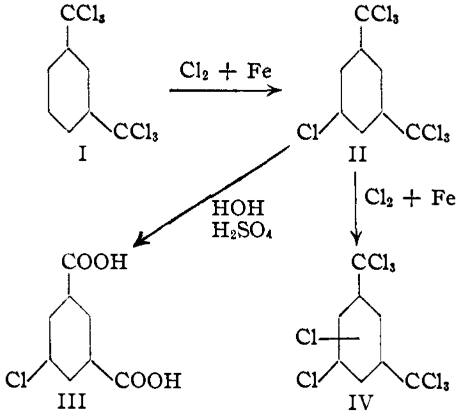
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF DUKE UNIVERSITY]

Chloro- and Dichloro-*bis*-(trichloromethyl)-benzenes[1]

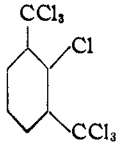
BY C. K. BRADSHER, P. M. GROSS, M. E. HOBBS, R. S. KITTILA, L. RAPOPORT,[2] P. TARRANT[3] AND G. WEST[4]

In the course of a program of indirect fluorination carried out in this laboratory, it became necessary to prepare some *bis*-(trichloromethyl)-benzenes containing a chlorinated nucleus. A few such compounds have been mentioned previously, chiefly in the patent literature,[5,6,7,8,9] but with little information as to details of preparation or physical constants. A description of the preparation, physical constants, and, where possible, the proof of structure of some compounds of this class forms the subject of the present communication.

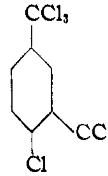
Our investigation followed two general lines, the nuclear chlorination of *bis*-(trichloromethyl)-benzenes and the chlorination of the methyl groups of chloroxylenes. In the nuclear chlorination of 1,3-*bis*-(trichloromethyl)-benzene (I), chlorine enters the position *meta* to the two trichloromethyl groups to yield the new 5-chloro-1,3-*bis*-(trichloromethyl)-benzene (II). Hydrolysis of the product yielded the known[10] 5-chloro-isophthalic acid (III).



Introduction of a second chlorine atom into the nucleus of 5-chloro-1,3-*bis*-(trichloromethyl)-benzene (II) or dichlorination of the parent 1,3-*bis*-(trichloromethyl)-benzene (I) alike yielded a viscous liquid which appears to be a dichloro-1,3-*bis*-(trichloromethyl)-benzene (IV). From several of the dichlorination runs there was isolated a small amount of a high melting solid which proved to be 2,5-dichloro-1,4-*bis*-(trichloromethyl)-benzene.[9]



V



VI

The 2-chloro- (V), 4-fluoro-,[11] and 4-chloro-1,3-*bis*-(trichloromethyl)- (VI) and 2-chloro-1,4-bis-(trifluoromethyl)-benzenes were prepared from the corresponding halogenated xylenes by chlorination at elevated temperatures in the presence of a mercury arc, and using the patented technique[6b] of employing a large excess of chlorine in the latter stages. It was found that the 4-chloro-1,3-*bis*-(trichloromethyl)-benzene (VI) obtained from monochlorinated meta-xylene had to be separated from a small amount of the 2-isomer (V). This suggests that nuclear chlorination of the hydrocarbon yields a mixture containing the 2- as well as the 4-isomer, a result that would be predicted by ordinary rules of orientation, but which seems to have escaped earlier workers.[12]

Experimental

5-Chloro-1,3-*bis*-(trichloromethyl)-benzene (II).—A glass reactor was charged with 243 g. of 1,3-*bis*-(trichloromethyl)-benzene[6b] (m. p. 32–36°) and 0.25 g. of iron filings. The reactor was heated to 115–125° and a rapid stream of chlorine bubbled through the liquid for five hours. At the end of this time, the weight increase amounted to 15% more than the theoretical. The fraction distilling at 150–169° (6–7 mm.) amounted to 163 g. and partly solidified on cooling. Recrystallization of the solid portion from alcohol yielded 73 g. of white flakes, m. p. 76–78°. An analytical sample (m. p. 77–78°) gave low values for chlorine, but its identity was established by hydrolysis to 5-chloro-isophthalic acid.

Anal. Calcd. for $C_8H_3Cl_7$: Cl, 71.5. Found: Cl, 71.0.

5-Chloro-isophthalic Acid (III).—The above compound (II) was heated with 100 ml. of 85% sulfuric acid. As the temperature neared the boiling point of the acid,

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(5a) Since this manuscript was submitted, but before it was accepted for publication, McBee, Bolt, Graham and Tebbe, THIS JOURNAL, **69**, 947 (1947) have described 4-chloro-1,3-bis-(trichloromethyl)-benzene. The 2-chloro-1,3-bis-(trichloromethyl)-benzene was also prepared but seems not to have been isolated in pure form. No constants are reported for the latter compound.

(5) (a) French Patent 663,791. (b) *Chem. Zentr.*, **100**, II, 2731 (1929).

(6a) U. S. Patent 2,005,712; *ibid.*, **107**, I, 876 (1936).

(6b) French Patent 798,727; *ibid.*, **107**, II, 3360 (1936).

(6c) U. S. Patent 2,132,361; *ibid.*, **109**, II, 4363 (1938).

(7) British Patent 464,859; *ibid.*, **108**, II, 4444 (1937).

(8) French Patent 820,696; *ibid.*, **109**, I, 1661 (1938).

(9) Ruggli and Brandt, *Helv. Chim. Acta*, **27**, 274 (1944); *C. A.*, **38**, 6288 (1944).

(10) Beyer, *J. prakt. Chem.*, [2] **25**, 465 (1882); *cf.* Klages and Knoevenagel, *Ber.*, **28**, 2044 (1895).

(11) We are indebted to Dr. Frances Brown of this Laboratory for the preparation of a quantity of 4-fluoro-1,3-dimethylbenzene from the corresponding amine by diazotization in liquid hydrogen fluoride.

(12) *Cf.* Jacobsen, *Ber.*, **18**, 1760 (1885).

the evolution of hydrogen chloride commenced and proceeded vigorously for several minutes. After cooling, the mixture was poured into a large volume of water and the solid collected. The acidic material was dissolved in sodium carbonate, treated with charcoal, filtered and reprecipitated by addition of concentrated hydrochloric acid. After drying at 120° the white powder melted at 279–280° (lit.[10] 278°). Neutral equivalent calcd. for $C_8H_5O_4Cl$: 100.3. Found: 105, 104.

The dimethyl ester was obtained as white needles, m. p. 79–80°.

Anal. Calcd. for $C_{10}H_9O_4Cl$: Cl, 15.51. Found: Cl, 15.59.

The ethyl ester melted at 50–51° (lit.[10] 45°).

Dichlorination of 1,3-*bis*-(Trichloromethyl)-benzene.—The chlorination was carried out essentially as described above for the preparation of the 5-chloro-1,3-*bis*-(trichloromethyl)-benzene except that chlorination was continued for ten hours, and the temperature was allowed to go as high as 145°. From 204 g. of *bis*-(trichloromethyl)-benzene, 138 g. of a very viscous liquid was obtained b. p. 184–189° (9 mm.). Essentially the same result was obtained by starting with 5-chloro-1,3-bis-(trichloromethyl)-benzene.

Anal. Calcd. for $C_6H_2Cl_2(CCl_3)_2$: active Cl,[13] 55.9. Found: active Cl, 55.4.

In the dichlorination of *bis*-(trichloromethyl)-benzene prepared from research grade *m*-xylene (E. K. 275), a small quantity of a high melting isomer, m. p. 191–192°, was obtained. This was shown to be 2,5-dichloro-1,4-*bis*-(trichloromethyl)-benzene (lit.[9] 193°).

Anal. Calcd. for $C_8H_2Cl_8$: Cl, 74.3. Found: Cl, 74.8.

2-Chloro-1,3-*bis*-(trichloromethyl)-benzene (V).—The chlorination of 179 g. of 2-chloro-1,3-dimethylbenzene[14] (b. p. 181.5–183°; n^{25}_D 1.5241) was carried out at 120–130° in a glass reactor and in the presence of a mercury arc. After the theoretical quantity of chlorine had been absorbed (fifteen hours), the mixture was cooled and the crude crystals collected, m. p. 115–125°; yield 130 g. (30%). On recrystallization from ethanol, white prisms were obtained, m. p. 136–137°.[15]

Anal. Calcd. for $C_8H_3Cl_7$: Cl, 71.5. Found: Cl, 71.5.

4-Chloro-1,3-*bis*-(trichloromethyl)-benzene (VI).[6b,6c]—The chlorination of 166 g. of 4-chloro-1,3-dimethylbenzene (b. p. 181–184°, n^{17}_D 1.5269) under similar conditions to those used in the preparation of the 2-isomer yielded 177.5 g. (50%) of 4-chloro-1,3-*bis*-(trichloromethyl)-benzene as a viscous liquid, b. p. 180–185° (8.5 mm.).

Anal. Calcd. for $C_8H_3Cl_7$: Cl, 71.5. Found: Cl, 71.0, 71.5.

The residue from the distillation of 4-chloro-1,3-*bis*-(trichloromethyl)-benzene yielded a small quantity of solid which was identical with the 2-chloro-1,3-bis-(trichloromethyl)-benzene (VI) described above and gave no depression of melting point when mixed with it.

4-Fluoro-1,3-*bis*-(trichloromethyl)-benzene.—The chlorination of 4-fluoro-1,3-*bis*-(trichloromethyl)-benzene[16] was carried out essentially as described for the chloro compounds above, twenty-eight hours being required. Vacuum distillation gave an 82% yield of a colorless oil, b. p. 157.5–159.5° (11 mm.).

Anal. Calcd. for $C_8H_3Cl_6F$: Cl, 64.3. Found: Cl, 64.4, 64.5.

2-Chloro-1,4-*bis*-(trichloromethyl)-benzene[5] was prepared in 79% yield by side-chain chlorination of 2-chloro-*p*-xylene in the manner described above, the crude chlorination product being purified by recrystallization from ethanol, m. p. 78–80°.

Anal. Calcd. for $C_8H_3Cl_7$: Cl, 71.5. Found: Cl, 71.4.

Summary

Some bis-(trichloromethyl)-benzenes containing nuclear halogen have been prepared, and some evidence has been obtained in support of the assigned structures.

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[13] The compound was refluxed for eighteen hours with a mixture of 10 ml. of 15% potassium hydroxide solution and 20 ml. of ethanol. After acidification, the chloride ion was determined by the Volhard method.

[14] U. S. Patent 1,796,108; *C. A.*, **25**, 2441 (1931).

[15] This compound has been prepared previously (ref. 6a) but no constants were given.

[16] Balz and Schiemann, *Ber.*, **60**, 1186 (1927).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF DUKE UNIVERSITY]

Chlorination of 1,3-bis-(Trifluoromethyl)-benzenes[1a,b]

BY CHARLES K. BRADSHER AND RICHARD S. KITTILA

In an investigation of methods for the preparation of *bis*-(trifluoromethyl)-benzenes containing nuclear chlorine,[2] the direct chlorination of *bis*-(trifluoromethyl)-benzenes was studied. Recently McBee, Hass, Weimer, Burt, Welch, Robb and Speyer[3] have reported that chlorination in the presence of conventional catalysts, and at temperatures approaching the boiling point of *bis*-(trifluoromethyl)-benzenes is without effect, and this is confirmed by our observations. While it was stated that chloro-*bis*-(trifluoromethyl)-benzenes could be obtained by reaction in the vapor phase at 500°, it was added that "at this high temperature there was extensive chlorinolysis."[4]

We have found that chlorination of *bis*-(trifluoromethyl)-benzenes may be effected readily by carrying out this reaction in an iron reactor at 150–170° and under a chlorine gage pressure of 300 lb./sq. in.

The material used in the majority of our chlorination experiments was a mixture containing both

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[1a] This work was sponsored by the Naval Research Laboratory.

[1b] With the exception of the experiment noted, the material contained in this communication is drawn from a thesis submitted to the faculty of the Graduate School of Arts and Sciences for the degree of Master of Arts, November, 1943.

[2] *Cf.* Bradsher, Gross, Hobbs, Saylor, Tarrant and West, Abstracts of Papers Presented Before the Division of Organic Chemistry at the 111th Meeting of the American Chemical Society, April, 1947.

[3] McBee, Hass, Weimer, Burt, Welch, Robb and Speyer, *Ind. Eng. Chem.*, **39**, 387 (1947).

[4] No yields have been mentioned, and it is clear from the text that this process was abandoned as unworkable.