values for the bond angle. Smith[13] has calculated from the molecular moment of inertia of cyclopropane (obtained from analysis of the fine structure of the infrared spectrum) an angle of 136°, corresponding to a tetrahedral C–C–H angle; Donahue, Humphrey and Schomaker,[14] from electron diffraction studies of the similar spiropentane structure, have suggested a 120° H–C–H angle (which makes the C–C–H angle 115.5°). In view of the conflicting results which have been thus variously derived, a more accurate direct determination of the external valence angle of cyclopropane would be of interest.

One consideration which supports the small value of the bond angle indicated here is that, according to Dennison,[15] in the vibration spectrum of methane, the mode of vibration corresponding to simultaneous mutual approach of two pairs of hydrogen atoms has a lower frequency than the mode corresponding to alternate approach of the pairs. This would seem to indicate that a strain on one pair of tetrahedral bonds tending to decrease the angle between them (as in cyclopropane) also decreases the equilibrium value of the other bond angle. (In double bonded compounds such as ethylene, this effect may be counteracted by shortening of the bond distances.)

The value of 1.76 Debyes for the dipole moment of monochlorocyclopropane, midway between the single bond moment of a paraffinic carbon–chlorine bond (2.04)[16] and of an olefinic carbon–chlorine bond (*ca.* 1.5) is in harmony with the apparent inertness of the chlorine attached to the cyclopropane ring, and it is possible that the substituent reactivities of isopropyl chloride, chlorocyclopropane, and vinyl chloride follow the same order as their dipole moments. In any case, the intermediate value of the chlorocyclopropane is noteworthy.

Acknowledgment.—The author wishes to express his thanks to Dr. Herbert S. Harned, under whose direction these researches were undertaken, to Dr. P. G. Stevens for suggesting the study of the cyclopropane derivatives, and to Dr. Lars Onsager for his advice in regard to the theoretical discussion of the problem.

Summary

1. The dipole moments of chlorobenzene, 1,2-*dl*-dichlorocyclopropane, and monochlorocyclopropane have been measured in benzene at audio frequencies by a bridge method.

2. The structure of the above-mentioned dichlorocyclopropane has been found to be *dl*, and the external valence angle of the cyclopropane ring has been calculated from the dipole moment data.

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[13] Smith, *Phys. Rev.*, (2) **59**, 924 (1941).

[14] Donahue, Humphrey and Shomaker, THIS JOURNAL, **67**, 332 (1945).

[15] Dennison, *Rev. Mod. Phys.*, **12**, 206 (1940).

[16] C. P. Smyth, "Dielectric Constant and Chemical Structure," Chem. Cat. Co., New York, N. Y., 1931; Appendix.

NEW HAVEN, CONN. RECEIVED SEPTEMBER 24, 1945

[CONTRIBUTION FROM THE STERLING CHEMICAL LABORATORY OF YALE UNIVERSITY]

Some New Cyclopropanes with a Note on the Exterior Valence Angles of Cyclopropane

BY PHILIP G. STEVENS[1]

The reaction of cyclopropane with chlorine is mainly that of substitution.[2] The initial product, monochlorocyclopropane, however, reacts so readily with more chlorine that, unless special procedures are adopted,[3] the cyclic products actually isolated consist almost entirely of dichlorides, the 1,1 and the 1,2 in the approximate ratio of 40:1. This great preponderance of 1,1 over 1,2-chlorination is a notable exception to the Meyer–Herzfelder rule,[4] and also to the results of both Tischenko[5] (using chlorine) and Kharasch and Brown[6] (using sulfuryl chloride) with *n*-butyl chloride, but is in harmony with the high temperature chlorination reported by Rust and Vaughan.[7] Both these two similar types of chlorination illustrate the increased activity of the hydrogen atom attached to a carbon atom holding a chlorine atom, which activity becomes effective when no steric hindrance is present as in the cyclopropane derivatives, or is reduced to a minimum at the elevated temperature employed by Rust and Vaughan.

The 1,2-dichloride does not seem to have been described previously, although Petrenko–Kritschenko[8] reported its reaction with alkali. It is stable to bromine and permanganate, to zinc dust in boiling acetic acid, and gives no color with tetranitromethane. Attempts to determine the configuration by chromatographical resolution using sucrose were unsuccessful. Spinrad[9] however has shown from the dipole moment that it must have the *dl*-configuration, and that the angle α of the carbon–chlorine bond with the ring

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[2] Gustavson, *J. prakt. Chem.*, [2] **42**, 496 (1890); **43**, 396 (1891).

[3] Roberts and Dirstine, THIS JOURNAL, **67**, 1281 (1945).

[4] Herzfelder, *Ber.*, **26**, 2932 (1893).

[5] Tischenko, *C. A.*, **31**, 5754 (1937).

[6] Kharasch and Brown, THIS JOURNAL, **61**, 2142 (1939).

[7] Rust and Vaughan, *J. Org. Chem.*, **6**, 478 (1941).

[8] Petrenko-Kritschenko, *Ber.*, **62**, 589 (1929).

[9] Spinrad, THIS JOURNAL, **68**, 617 (1946).

plane appears to be 48°. This value would make the exterior angle (if 2α) of the cyclopropane 96°, a value in marked disagreement with figures reported by other investigators for cyclopropane itself. Unfortunately it was not possible to purify the dichloride further, and hence the small angle may be caused by impurities of high dipole moment. If, however, the dichloride is pure, the newly calculated angle is of great interest as explained in the footnote below.[10]

A study of atomic models, and a consideration of the increased stability of cyclopropane rings caused by electronegative groups[11] suggested that it should be possible to prepare higher chlorinated cyclopropanes. Accordingly the 1,1-dichloride was treated with sulfuryl chloride and benzoyl peroxide, but unlike cyclopropane or the monochloride, the dichloride reacted mainly by addition (ring opening), and gave only an 8–10% yield of the 1,1,2-trichloride. The other products were the hitherto unknown 1,1,1,3,3-pentachloropropane,[12] b. p. 179°, liquid at −78°, yield 45–50%, a polychloride thought to be the 1,1,1,3-tetrachloropropane[13] (also unknown), b. p. 156–157°, yield 15%, and a complex mixture of higher chlorides.

The structure of the pentachloride shows that the ring is opened by chlorine in a manner different from that assumed by Gustavson[2] for ring opening by bromine.

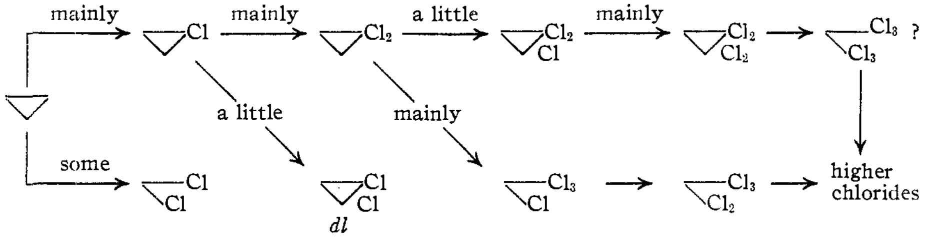
While no tetrachlorocyclopropane was isolated from the above reaction products, it was prepared in good yields by starting with the pure trichloride, the main reaction being then substitution. Attempts to prepare hexachlorocyclopropane from the pure tetrachloride using chlorine however failed,[14] the products being mainly hepta- and octachloropropane. A very small amount of a new chloride, m. p. 102°, was obtained but, as it contained some hydrogen, it was probably the unknown 1,1,1,3,3,3-hexachloride rather than the hexachlorocyclopropane.

The structures of the tri- and tetrachlorocyclopropanes were proved by their molecular refraction, analyses and inertness to typical ethylenic reagents.

TABLE I

Chlorocyclopropane	B. p., °C.	M. p., °C.	$n^{25}D$	d^{25}_4	MR Calcd.	MR Found	Exaltation
1,1-Di-	75.0	....	1.4377	1.2178	23.59	23.89	+0.30
dl-1,2-Di-	87.2	−19.5	1.4502	1.2492	"	23.87	+0.28
1,1,2-Tri-	124.2	−36.5	1.4782	1.4270	28.45	28.86	+0.41
1,1,2.2-Tetra-	145.8	−18.5	1.4976	1.5682	33.32	33.60	+0.28

It can be seen that except in the case of cyclopropane, substitution by chlorine on the ring predominates over addition (ring opening) only if a hydrogen atom on a tertiary carbon atom is available. The course of the chlorinations can be represented as follows:



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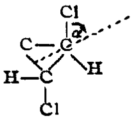
(10) This value of 48°, if correct, for the angle α, is rather surprising, and leads to some interesting considerations. Thus the angle



C–C–Cl becomes 125.3° (I am indebted to Dr. Spinrad for this calculated value), which is not far different from the corresponding angle of 122.5° of *trans* dichloroethylene (Brockway, Beach and Pauling, THIS JOURNAL, **57**, 2693 (1935)). The angle Cl–C–H however, *if assumed to be 2α*, becomes only 96°, which is considerably less than the value 115°, computed on the above same assumption, for the Cl–C–H angle of *trans* dichloroethylene.

Of course the size of the Cl–C–H angle in the ethylene is not known yet, and it is possible that this same Cl–C–H angle in the cyclopropane is not 2α, but nearer to 115°, in which case the hydrogen atom would be compressed somewhat toward the ring plane. A value as large as 120°, which has been suggested for the H–C–H angle of spiropentane (Donahue, Humphrey and Schomaker, THIS JOURNAL, **67**, 332 (1945)), would result in a H–C–C angle of 115.5° (I am indebted to Dr. Spinrad for this calculated value), and an angle of 136°, as computed by Smith (*Phys. Rev.*, [2] **59**, 924 (1941)) for cyclopropane from the moment of inertia would result in an even greater distortion. If however the angle Cl–C–H is 2α, then the exterior angle of 96° is much smaller than any previously considered, and *if normal* for cyclopropane itself, would help explain the stability observed for spiropentane (Murray and Stevenson, THIS JOURNAL, **66**, 812 (1944)). This is because the compression of the valence angle of the central carbon atom of spiropentane would then be only 96–61° or 35°, instead of 48° if 2α equals 109°, or the extreme compression of 75°, if 2α equals 136°.

(11) That chlorine can function as a stabilizing group like the carbonyl group is shown by the inertness of the 1,1-dichloride to concentrated hydrochloric acid at 108° for nine days, whereas cyclopropane reacts at a measurable rate at room temperature.

(12) The pentachloride structure is based on the fact that its physical properties are different from any of the four other isomers:—the 1,1,1,2,3 being a solid, m. p. 179° (Victoria, *Rec. Trav. Chim.*, **24**, 265 (1905)), the 1,1,2,2,3 boiling at 191° (hitherto unknown but described in this paper), the 1.1,2,3,3 boiling at 198° (Prins, *J. prakt. Chem.*, [2] **89**, 414 (1914)), and lastly the 1,1,1,2,2 having been reported as a solid (Borsch and Fittig, *Ann.*, **133**, 116 (1865)). While these last workers did not fully characterize their pentachloride, the evidence for its structure seems secure, since the only other possible product they could have obtained was the 1,1,2,2,3 isomer, which is a liquid at −70°. Compare Szenic and Taggesell (*Ber.*, **28**, 2668 (1895)), and Spring and Lecrenier (*Bull. soc. chem.*, [2] **48**, 623 (1887)).

(13) The structure of the tetrachloride is uncertain. Attempts to purify it by distillation through a 50-plate Stedman column resulted in the formation of a trichloropropene.

(14) Substitution would be expected to be difficult due to the double vicinal effect (compare ref. 7).

Experimental

Chlorination of Cyclopropane.—The directions of Gustavson[2] were followed with a few modifications. Two five-liter flasks were connected by a large siphon tube reaching to the bottom of the reaction flask (round bottom), and to within a few cm. of the bottom of the second flask (erlenmeyer). After filling the reaction flask with water, about three liters of cyclopropane were admitted, the water displaced being forced through the siphon into the other flask. Five hundred ml. of chlorine was then admitted under illumination of a 100-watt bulb. The reaction was slow at first, but became faster as the temperature rose, the oily chloride formed sinking to the bottom. When the reaction was complete, more reactants were admitted, whereby the chloride formed was forced over into the second flask. The process was repeated, or the two gases admitted continuously, the only precaution necessary being that of keeping the cyclopropane always in considerable excess, or otherwise an explosion might occur. These explosions were however not very dangerous, for out of three such explosions, only one broke the reaction flask, and then not violently. The oily chloride was shaken with aqueous sodium carbonate solution, dried over anhydrous potassium carbonate, and fractionally distilled. From about 2.5 liters of crude chloride, there was obtained approximately 50 ml. of the monochloride, 1900 ml. of the 1,1-dichloride, 50 ml. of the *dl*-1,2-dichloride, and 500 ml. of higher boiling chlorides, mostly chloropropanes. Using a 50-plate Stedman column, the distillation curve showed no indication of any compounds in the range 43–113°, other than the above three cyclic chlorides.

For the bond moment measurement,[8] the monochloride was redistilled through a 100-plate Stedman column, b. p. 43.8° (770 mm.). For the dipole moment measurement,[9] the 1,2-dichloride, after the above distillation through the Stedman column, b. p. 86.8–87.2°, was shaken with aqueous potassium carbonate, dried over anhydrous potassium carbonate, and redistilled through a Claisen flask, b. p. 87.0–87.2° (757 mm.), m. p. about −19.5°. It[15] had a sweeter odor than the 1,1-isomer. *Anal.* Calcd. for $C_3H_4Cl_2$: C, 32.4; H, 3.60; Cl, 64.0. Found: C, 32.5; H, 3.53; Cl, 63.6.

Chlorination of the 1,1-Dichloride.—Chlorine at 63° under illumination of a 100-watt bulb reacted smoothly, but better results were obtained thus: a mixture of 275 ml. of the chloride, 150 ml. of sulfuryl chloride and 1.7 g. of benzoyl peroxide was heated to 78° under reflux for two to three days, adding an additional 1.7 g. of peroxide after the first day. After cooling, the reaction mixture was shaken with water (there was much unreacted sulfuryl chloride), with aqueous soda, dried over anhydrous potassium carbonate, and distilled, yielding about 160 ml. of unreacted chloride, and 100 ml. of chlorinated product. From 760 ml. of product the following fractions were obtained by distillation through a 50-plate Stedman column: A, 55 ml., 1,1,2-trichlorocyclopropane, b. p. 123.8–124.5° (mainly 124.2° at 763 mm.); B, 20 ml., b. p. 125–129°; changing now to a glass helix-filled column: C, 43 ml., b. p. 130–150°; D, 6 ml., b. p. 150–155°; E, 104 ml., b. p. 155–157.5°, presumably 1,1,1,3-tetrachloropropane; F, 30 ml., b. p. 157.5–176°; and G, 500 ml., residue. Another sample of the trichlorocyclopropane, prepared earlier boiled at 123.7–124°, and melted at about −36.5°. *Anal.* Calcd. for $C_3H_3Cl_3$: C, 24.8; H, 2.08; Cl, 73.2. Found: C, 24.9; H, 2.11; Cl, 72.9. The trichloride did not react with concentrated hydrochloric acid at 85° (four days in a sealed tube), with bromine in acetic acid or with permanganate.

The material, corresponding to the residue G, from an earlier preparation, was fractionally distilled, yielding mainly the 1,1,1,3,3-pentachloropropane, b. p. 178.5–179° (762 mm.), b. p. 61° (10 mm.). *Anal.* Calcd. for $C_3H_3Cl_5$: C, 16.6; H, 1.38; Cl, 82.0. Found: C, 16.8; H, 1.35; Cl, 82.1. The pentachloride had a camphoraceous odor and did not crystallize at −78°, $n^{25}\text{D}$ 1.4977, d^{25}_4 1.5839, *MR* calcd. 40.39, found 40.01.

Attempts to obtain some tetrachlorocyclopropane from fraction C by refractionation were unsuccessful, and a redistillation of fraction E through a 50-plate Stedman column resulted in complete decomposition into hydrogen chloride and an unsaturated polychloride b. p. 133–134°. The material boiling above the pentachloride yielded no definite products.

Chlorination of the 1,1,2-Trichloride.—This was carried out exactly as described above, except that the reaction mixture was heated for only one day. From each run of 30 ml. of trichloride, about 18 ml. were recovered and reused. The main product was 1,1,2,2-tetrachlorocyclopropane, b. p. 145.3–146.1°, there being a relatively small amount of higher boiling material, b. p. 150–200°. The tetrachloride was redistilled, the fraction, b. p. 145.8° (762 mm.) being deemed pure. It had an odor midway between carbon tetrachloride and camphor, absorbed no bromine in acetic acid, and reacted with aqueous permanganate only very slowly. *Anal.* Calcd. for $C_3H_2Cl_4$: C, 20.0; H, 1.12. Found: C, 20.3; H, 1.23.

Chlorination of the 1,1,2,2-Tetrachloride.—With chlorine at 63° under illumination of a 75-watt bulb, the reaction proceeded very slowly, hydrogen chloride being evolved. After five days, a few thin plates appeared in the upper part of the reaction vessel and, after seven days, the main product had solidified. The thin plates were removed mechanically, and recrystallized from 90% aqueous methanol from which they separated as quite volatile, long, thin, rectangular plates, m. p. 102–102.5°. *Anal.* Calcd. for $C_3H_2Cl_6$: C, 14.4; H, 0.80: for C_3Cl_6: C, 14.5; H, 0.00. Found: C, 15.1; H, 0.53. Attempts to obtain more of the 102° melting chloride failed, and lack of material prevented further investigation. Recrystallization of the main product from 90% methanol yielded octachloropropane; and distillation (b. p. mainly 235–268°) showed that the heptachloride was also present.

Preparation of 1,1,2,2,3-Pentachloropropane.—1,2,2,3-Tetrachloropropane[16] b. p. 161.0–161.7° (766 mm.) was treated with sulfuryl chloride as before, the reaction proceeding very slowly. The products were worked up as usual, and distilled. After the unreacted tetrachloride had been removed, the boiling point rose rapidly to 190° (no plateau at 179°). The pentachloride, b. p. 191–191.5° (755 mm.), $n^{25}\text{D}$ 1.5098, d^{25}_4 1.6326, had a pleasant camphoraceous odor, but was still slightly impure, as the chlorine content was somewhat low. It failed to solidify at −70°.

Summary

1. Three new chlorocyclopropanes, and two new pentachloropropanes have been prepared.

2. Except with cyclopropane, substitution of hydrogen by chlorine predominates over ring opening only when a hydrogen atom on a tertiary carbon atom is available.

3. The size of the angle (as determined by Spinrad) made by the chlorine atom of *dl*-1,2-dichlorocyclopropane with the ring plane, thus indicating a smaller exterior valence angle than previously considered for cyclopropane, has been discussed.

NEW HAVEN, CONN. RECEIVED AUGUST 25, 1945

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(15) Passage through a 208-cm. column of sucrose failed to achieve any resolution.

(16) From Halogen and Perfume Chemicals, Columbia, S. C.