

TABLE II
RESULTS FROM THE RAPID CHLORINATION OF DRIED SAMPLES

Sample	Boron I	"Pure" Boron	"99%" Boron
No. of determinations	4	3	7
Average residue, %	14.3	60.1	23.1
Upper and lower limits, %	15.4-13.4	60.9-59.0	24.4-22.1
Sublimed chlorides	Ferric, % Fe	0.6	1.8
	Aluminum, % Al	8.6	Trace
Composition of residue	Chloride, % Cl	Trace	19.8
	Magnesium, ^a % Mg	...	6.8
	Boric oxide, ^b % B ₂ O ₃	None	8.5
Spectrographic report on residue	Appreciable	B, Na, Al, Si	B, Mg, Si
	Traces	Ca, Mg	Mn, Cu, Ca

^a Calculated from results of chloride determination. Qualitative tests showed magnesium present in approximately the expected amounts. ^b Boric oxide reported here is that extracted by hot water.

Slow chlorination.—Additional information was sought by chlorinating more slowly 100-mg. samples of boron in a horizontal reaction train. The less volatile reaction products, such as ferric and aluminum chlorides, condensed in the train before they reached two gas washing bottles, which contained water initially. Boron trichloride was absorbed and hydrolyzed in these washing bottles, the solutions in which were eventually titrated for hydrochloric and boric acids; the glass electrode was used here also.

Despite space limitations, it seems well to point out that chlorine can complicate these acid determinations in several ways. These complications were finally minimized by wrapping the washing bottles with black cloth (to prevent photochemical reactions during the chlorination); by shaking the solution from a washing bottle with excess mercury (to extract the residual chlorine), mercury and mercurous chloride being removed and washed before the solution and washings were titrated; and by carrying out the chlorine extraction immediately a run was finished. Runs made without boron showed blank corrections to be small.

The results of this work are given in Table III. The residues were usually light gray.

TABLE III

SLOW CHLORINATION DATA FOR DRIED 100-MG. SAMPLES

	Boron I		"Pure" Boron		"99%" Boron	
BCl ₃ liberated, as						
% B	59.0	56.7 55.8	60.5 65.5	59.7 62.3		
% Residue ^a	..	20.8 22.5	59.2 56.8	23.1 21.9		
Moles HCl/moles H ₃ BO ₃	3.16	3.05 3.17 ^b	2.95 3.01 ^b	2.83 3.00 ^b		

^a Residues should have compositions corresponding to those of Table II. ^b Obtained by final, improved method.

Boron trichloride seems to be the only boron compound and the only acid-producing substance reaching the washing bottles in appreciable amount. (In all our chlorination work, the sublimed reaction products could have included small amounts of volatile boron compounds.) We believe that Table III truly gives the percentage of the sample converted to boron trichloride; this percentage is in every case appreciably smaller than the per cent. total boron in Table I; it probably includes all the boron present as the element and as metallic borides.

According to Table II, the percentage of the samples volatilized out of the test-tube during rapid chlorination is $100 - (14.3 + 0.6 + 8.6) = 76.5$ for Boron I; $(100 +$

$19.8) - (60.1 + 1.8) = 57.9$ for "Pure" Boron; and 91.6 for "99%" Boron. For "Pure" Boron, this percentage agrees with the % B in Table III; but in the other cases it is appreciably greater.

Spectrographic examination of our samples showed carbon to be absent. The analytical results (Tables I and II) show that some element (presumably oxygen) not listed in Table II must be present in appreciable amount. The data of the preceding paragraph point to a possible volatilization of lower boron oxides or oxychlorides during the chlorination of Boron I and of "99%" Boron; that this could have escaped observation has been mentioned.

As a matter of historical interest, we examined the small quantity available of a pinkish beige powder¹ labeled "Weintraub B₂O 1908." Fusion gave 76.3% total boron. Rapid chlorination gave 3.4% residue, 0.06% iron. Spectrographic report on the residue: B, high; Si, present; Mg, trace. We do not consider that the existence of B₂O has been established.

We wish to emphasize finally that materials sold commercially as pure boron may contain less than 80% total boron, much of which is not present as the element. The most likely impurities are oxygen and whatever reducing agent (in our cases, magnesium, aluminum) was used in the preparation. We hope that the methods outlined here will prove useful in further work on the problems of crude boron.

(1) Cf. Weintraub, *Trans. Electrochem. Soc.*, **16**, 165 (1909).

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NEW COMPOUNDS

sym-p,p'-Dichlorotetraphenylethylene

Treatment of 100 g. of *p*-chlorobenzophenone with 100 g. of phosphorus pentachloride at 150° according to Overton¹ yielded 110 g. (90%) of *p*-chlorobenzophenone chloride;

(1) Overton, *Ber.*, **26**, 28 (1893).

b. p. 189–194^o (12 mm.); d^{20}_4 1.302; n^{20}_D 1.6110. Attempts to convert this chloride to the desired ethylene by treatment with sodium iodide in dry acetone yielded a mixture of crystalline compounds which could not be separated by repeated recrystallizations. Analysis indicated the product to be a mixture of the two pinacolones,

$\text{C}_6\text{H}_5\text{C}(\text{O})\text{C}(\text{C}_6\text{H}_5\text{Cl})_2$ and $\text{ClC}_6\text{H}_4\text{C}(\text{O})\text{C}(\text{C}_6\text{H}_5)_2$, in spite of precautions to exclude moisture. From 63 g. of *p*-chlorobenzophenone chloride and 70 g. of sodium iodide boiled under reflux in 500 cc. of dry acetone for twelve hours, 45 g. of the mixture was obtained, m. p. 126–145°. After repeated recrystallization a sample melted at 130–142°.

Anal. Calcd. for $\text{C}_{26}\text{H}_{18}\text{Cl}_2\text{O}$: C, 74.82; H, 4.35. Found: C, 75.09; H, 4.39.

The desired ethylene was obtained by boiling 5 g. of *p*-chlorobenzophenone chloride in 50 cc. of dry ether with 10 g. of pure zinc dust for one hour. The mixture was filtered, washed with dilute hydrochloric acid, alkali and water and dried over calcium chloride. The ether was evaporated and the solid residue was extracted twice with 20-cc. portions of boiling alcohol. The residue was then crystallized several times from 50 cc. of alcohol to yield 0.5 g. (12%) of *sym-p,p'*-dichlorotetraphenylethylene, m. p. 202–203°.

Anal. Calcd. for $\text{C}_{26}\text{H}_{18}\text{Cl}_2$: C, 77.81; H, 4.52. Found: C, 77.85; H, 4.56.

When 0.25 g. of the ethylene in 10 cc. of benzene and 10 cc. of absolute alcohol was treated with 1 g. of sodium, a quantitative yield of fine white needles of tetraphenylethane was obtained, m. p. 209°.³

Anal. Calcd. for $\text{C}_{26}\text{H}_{22}$: C, 93.37; H, 6.63. Found: C, 92.89; H, 6.80.

Reduction of 1.1 g. of the ethylene in 15 cc. of methylcyclohexane with hydrogen at 110 atm. and 100° using 2 g. of Raney nickel as a catalyst yielded a mixture of products from which 0.3 g. of fine white needles of *p*-chlorotetraphenylethylene was isolated by recrystallization from aqueous acetic acid. The product melted sharply at 168°; Bergmann and Christiani⁴ report 165–166° and Norris and Tibbetts,⁵ 162°.

Anal. Calcd. for $\text{C}_{26}\text{H}_{19}\text{Cl}$: C, 85.11; H, 5.22. Found: C, 85.28; H, 5.43.

(2) Overton¹ reports the boiling point as 192° (12 mm.); Morgan (THIS JOURNAL, **38**, 2100 (1916)) reports 190° (10–12 mm.); and Ingold and Wilson (*J. Chem. Soc.*, 1493 (1933)) report 191–193° (13 mm.).

(3) Sagumenny, *Ann.*, **184**, 177 (1877).

(4) Bergmann and Christiani, *J. Chem. Soc.*, 412 (1936).

(5) Norris and Tibbetts, THIS JOURNAL, **42**, 2085 (1920).

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dl- and *meso*- γ,γ' -Diphenyl- γ,γ' -suberodilactone

The reduction of β -benzoylpropionic acid with zinc dust in boiling 80–90% acetic acid has been found to yield γ -

phenyl- γ -butyrolactone, m. p. 35–36°, in 30–40% yield accompanied by the corresponding bimolecular reduction products, the two stereoisomeric γ,γ' -diphenyl- γ,γ' -suberodilactones, in 12–17% yields. For example, 16 g. of β -benzoylpropionic acid in 75 cc. of 80% acetic acid was boiled for three and one-half hours while 25 g. of zinc dust was added in portions. The hot mixture was filtered and the cake of zinc dust was extracted with several portions of hot acetic acid to remove the high-melting dilactone. After several recrystallizations from glacial acetic acid, 1.5 g. (9%) of high melting dilactone was obtained, m. p. 267°.¹

On cooling the filtered reaction mixture, zinc acetate crystallized. This was removed by filtration and water was added. Crystalline dilactone and oily lactone separated from solution. Filtration yielded 1 g. (6%) of low-melting dilactone. After repeated recrystallization from alcohol, various samples showed a characteristic behavior in that they melted sharply at 165° to a cloudy semi-liquid which changed to a clear liquid sharply at 175.5°.

Anal. Calcd. for $\text{C}_{20}\text{H}_{18}\text{O}_4$: C, 74.57; H, 5.63; sapn. eq., 161. Found (267°): C, 74.55; H, 5.58; sapn. eq.,² 162. Found (165°): C, 74.34; H, 5.65; sapn. eq.,² 164.

(1) Fieser ("Organic Syntheses," Vol. XV, John Wiley and Sons, Inc., New York, N. Y., 1935, p. 65) has reported the isolation of γ,γ' -diphenyl- γ,γ' -suberodilactone, m. p. 254°, as a by-product of the Clemmensen reduction of β -benzoylpropionic acid.

(2) Redemann and Lucas, *Ind. Eng. Chem., Anal. Ed.*, **9**, 521 (1937).

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A Dioxanate of Iodine Pentafluoride

Iodine pentafluoride is partially soluble in dry 1,4-dioxane, addition of an excess causing colorless crystals of a dioxanate of formula $\text{IF}_5\cdot\text{C}_4\text{H}_8\text{O}_2$ to precipitate. The crystals start to hydrolyze immediately upon contact with the atmosphere, yielding iodic acid as the only solid residue after complete hydrolysis. They are likewise hydrolyzed over sulfuric acid in a desiccator.

When placed upon a melting point block, the dioxanate melts after an interval of time as low as 84°, but on immediate contact with the block only at 112° or above. In all cases melting is accompanied by decomposition and the evolution of hydrogen fluoride and purple iodine fumes.

Analysis was conducted by a modification of the method of Prideaux¹ (samples being weighed by shaking from a weighing bottle). Calculated for $\text{IF}_5\cdot\text{C}_4\text{H}_8\text{O}_2$: IF_5 , 71.6. Found: IF_5 , 69.9.

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