TABLE I

YIELD, PROPERTIES, AND COMPOSITION OF ALDOSE PHENYLBORONATES

bis(Phenylboronate)[a] of:	Yield, %	M.p., °C.[b]	$[\alpha]^{25}_{D}$, C_6H_6,*c*, <5	Formula	C		H		B		Phenylboronic acid,[d] millimoles/g.	
					Calc'd	Found[c]	Calc'd	Found[c]	Calc'd	Found[c]	Calc'd	Found
L-Arabinose[e]	45	166	+ 8.5°	$C_{17}H_{16}B_2O_5$	63.43	63.55	5.01	5.04	6.72	6.85	6.21	6.23
D-Ribose	24	140–142	+116	$C_{17}H_{16}B_2O_5$	63.43	63.66	5.01	5.00	6.72	6.52	6.21	6.22
D-Xylose	41	137	− 8.5	$C_{17}H_{16}B_2O_5$	63.43	63.58	5.01	4.93	6.72	6.77	6.21	6.21
D-Lyxose	25	109–110	− 60.4	$C_{17}H_{16}B_2O_5$	63.43	63.55	5.01	5.09	6.72	6.73	6.21	6.20
L-Fucose	30	109.5	+ 29.4	$C_{18}H_{18}B_2O_5$	64.35	64.45	5.39	5.42	6.44	6.61	5.95	5.96
L-Rhamnose[e]	35	107.5	+ 87	$C_{18}H_{18}B_2O_5$	64.35	64.43	5.39	5.36	6.44	6.64	5.95	5.99

[a] On qualitative paper chromatograms (Whatman paper No. 1, butanol:ethanol:water/40:11:19, silver nitrate-ammonia spray indicator), every ester showed decomposition into phenylboronic acid and the original sugar (identified by comparison with authentic specimens). [b] Kofler stage melting point. [c] Analyses by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.; dried to constant weight at 45° and 1–2 mm. [d] Method of Kuivila and co-workers, ref. 4. [e] Mol. wt. (cryoscopic in benzene): 309 for L-arabinose *bis*(phenylboronate) (calc'd, 322); 321 for L-rhamnose *bis*(phenylboronate) (calc'd, 336); determined by Mr. J. B. Miller of this Laboratory.

type of derivative in this field. The present communication reports the preparation of crystalline esters of phenylboronic acid with all of the pentose structures and with the two 6-deoxyhexoses L-fucose and L-rhamnose (Table I). The procedure of Kuivila, Keough, and Soboczenski,[4] while suitable for the acyclic alditols, failed to yield isolable crystalline products with the cyclic sugar structures. The present authors obtained phenylboronates of cyclic sugars by fusion techniques followed by product isolation with hydrocarbon solvents. The crude reaction product appeared to be a mixture from which a pure individual substance was obtained, on repeated crystallization, in yields of 24–45%. The products, so isolated and purified, were *bis*(phenylboronates) in which all four of the available hydroxyl groups were presumably esterified.

All of the products characterized were well crystallized and were stable in air. They were soluble in hydrocarbon solvents and were best recrystallized from petroleum ether. On the addition of water to their alcoholic solutions, the compounds were decomposed into their components, detectable by paper chromatography. The *bis*(phenylboronate) of L-arabinose was so hydrolyzed and the products obtained were identified by isolation methods. While not established, it is probable that this process involved a trans-esterification in the alcohol followed by hydrolysis, on the addition of water, of the dialkyl phenylboronate formed.

EXPERIMENTAL

Preparation of aldose bis(*phenylboronates*). An amount of 4.0 millimoles (0.60 g. of pentose, 0.66 g. of 6-deoxyhexose) of aldose and 8.0 millimoles (0.98 g.) of phenylboronic acid[5] were placed in a 50 ml. round-bottomed flask which then was evacuated to 10–15 mm. The mixture was heated slowly to fusion (110–160°) and maintained in the fused condition for 1 to 3 min. After cooling, 30–40 ml. of petroleum ether (b.p. 65–110°) was added and the mixture was refluxed, with stirring, for 10 min. and then was filtered through a fritted glass filter. This extraction was repeated with two further 20-ml. portions of petroleum ether. The combined filtrates were concentrated to 15–30 ml. The derivatives crystallized on allowing the concentrates to stand first at 30° and then, without filtering, at 0°. The crystals were removed and recrystallized six to eight times from hot petroleum ether to constant melting point. Data on the substances synthesized are recorded in Table I. The crystals were soluble in benzene, ether, methanol, ethanol and in warm petroleum ether; they were insoluble in water.

Hydrolysis of L-arabinose bis(*phenylboronate*). An amount of 400 mg. of L-arabinose *bis*(phenylboronate) was dissolved in 50 ml. of boiling methanol, 50 ml. of water was added, and the solution was concentrated under reduced pressure to remove the methanol. The cooled solution was extracted with ether and the residue obtained on solvent removal from the dried ether extract was crystallized from water and identified as phenylboronic acid by melting point, mixture melting point (217°) and paper chromatographic behavior (footnote *a*, Table I). The ether-extracted aqueous solution was concentrated to dryness under reduced pressure and the residue, crystallized from water-methanol, was identified as arabinose by melting point, mixture melting point (160°), and paper chromatographic behavior (footnote *a*, Table I).

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[5] Bean and Johnson, *J. Am. Chem. Soc.*, **54**, 4415 (1932).

Cyclopropanes. XXI.[1]

1-Acetyl-2-nitro-2,3,3-trimethylcyclopropane

LEE IRVIN SMITH AND W. L. KOHLHASE

Received March 22, 1956

As a part of a study of the action of bases upon nitrocyclopropyl ketones,[2] the preparation of the first two examples (Ia and Ib) of a nitrocyclopropyl ketone having only a single ring hydrogen atom was undertaken. Action of bases upon these 1-

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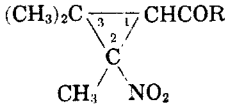
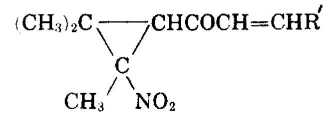
[1] Paper XX, Smith and Scribner, *J. Am. Chem. Soc.*, **78**, 3412 (1956).

[2] Paper XIX, Smith, Brotherton, and Kohlhase, *J. Am. Chem. Soc.*, **78**, 2532 (1956).

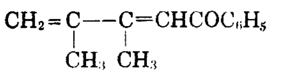
acyl-2-nitro-2,3,3-trimethylcyclopropanes (Ia and Ib) resulted in formation of two types of products from each—one base-soluble, the other, base-insoluble. Cyclopropane Ia produced large amounts of high-boiling material, distributed between both types of products, and it appeared that these may have been derived in part from condensation reactions of the α-methyl group, since ketone Ia readily underwent condensation at the α-methyl group with aromatic aldehydes to give compounds of structure II. Production of the high-boiling materials greatly complicated the study of the reaction between the methyl ketone (Ia) and basic reagents; this part of the study was therefore abandoned and attention was devoted to the cleavage reactions[2] of the phenyl ketone (Ib), which did not produce high-boiling by-products. The reaction of the phenyl ketone (Ib) with alkoxides, reported in detail in a previous paper,[2] produced as the chief base-insoluble product, 1-benzoyl-2,3-dimethylbutadiene (III). The base-soluble products were very unstable, but 3-methyl-5-phenylisoxazolone (IV) was isolated from this mixture.



Ia, R = CH_3
Ib, R = C_6H_5

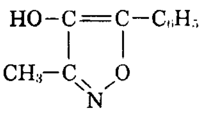


IIa, R′ = m-$NO_2C_6H_4$—
IIb, R′ = —$CH{=}CHC_6H_5$



$$\underset{\displaystyle CH_3}{\overset{}{CH_2{=}\underset{|}{C}}}{-}{-}\underset{\displaystyle CH_3}{\underset{|}{C}}{=}CHCOC_6H_5$$

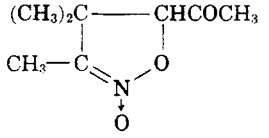
III



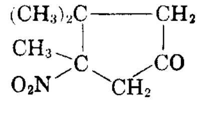
IV

This note describes the preparation and certain properties of 1-acetyl-2-nitro-2,3,3-trimethylcyclopropane (Ia). It was synthesized from mesityl oxide *via* a standard sequence of reactions originated by Kohler.[3] Addition of nitroethane to mesityl oxide proved difficult, and the yield of 4,4-dimethyl-5-nitro-2-hexanone never exceeded 21%. Diethylamine[4] was found to be the best catalyst. Others tried included sodium methoxide, calcium hydride,[5] piperidine, and "Triton B". Bromination of the adduct and subsequent ring closure by action of potassium acetate gave Ia in an over-all yield of 70% for these two steps.

The methyl ketone (Ia) gave positive tests for both a nitro group and an acetyl group. That the ketone was not the isomeric isoxazoline oxide (V) was shown by its failure to evolve chloride when heated with phosphorus pentachloride.[6] The base-catalyzed reaction of Ia with two moles of an aromatic aldehyde gave only a 1:1 condensation product (II). Failure to obtain any 1:2 product eliminated VI as the structure for the nitro ketone.



V



VI

Efforts to oxidize the methyl ketone (Ia) to the corresponding carboxylic acid by King's method[7] failed, although the intermediate pyridinium iodide was easily prepared.

Preliminary attempts to isolate individual compounds from the base-insoluble products of the alkaline degradation of Ia were not fruitful. However, fractional crystallization of a mixture of 2,4-dinitrophenylhydrazones obtained from the distillable portion of the base-insoluble products yielded a derivative analyzing properly for the 2,4-dinitrophenylhydrazone of a compound, $C_8H_{12}O$. This compound may be the acetyl analog of 1-benzoyl-2,3-dimethylbutadiene (III) obtained from Ib.

EXPERIMENTAL

All melting points are uncorrected. Microanalyses are by B. K. Davis, R. E. Kelly, and E. L. Wheeler.

4,4-Dimethyl-5-nitro-2-hexanone. A solution of nitroethane (225.2 g., 3.0 moles), mesityl oxide (294.4 g., 3.0 moles), and diethylamine (21.93 g., 0.30 mole) in dry methanol (300 cc.) was refluxed for 183 hours. The solvent and unchanged reactants were removed under reduced pressure (1.1 mm. at 55°). The residual brown liquid (204.4 g.) was a mixture containing 4-diethylamino-4-methyl-2-pentanone.[4] The latter was removed by washing an ether solution (250 cc. of ether) of the crude product with 2 N hydrochloric acid (200 cc. and 100 cc.). The ether solution then was washed with aqueous sodium carbonate (90 cc., 1%), sodium bicarbonate (75 cc., 2.5%), and water (three 50-cc. portions), and dried ($MgSO_4$). The solvent was removed and the residue was distilled through a 4-inch Vigreux column at 0.3 mm. After a small forerun (2.5 g., n_D^{25} 1.4458) fractions were collected at 61–71° (27.9 g., n_D^{25} 1.4473) and at 71–74° (92.4 g., n_D^{25} 1.4498). A dark viscous residual oil (18 g.) remained. The first fraction and the forerun were combined and redistilled, giving 9.7 g. of material boiling up to 67° (0.20 mm.) and 15.1 g. (n_D^{25} 1.4502) at 66–68° (0.20 mm.). The combined weight (107.5 g.) of the last fractions represented at 20.7% yield. No improvement in yield resulted when a 2:1 molar ratio of nitroethane:mesityl oxide was used. A sample of the material, when redistilled four times, formed a pale yellow liquid with the following properties: b.p. 55.6–57.0° (0.10 mm.); n_D^{25} 1.4498; d^{25} 1.0443 g./cc.; and MR_D 44.56 (exaltation = 1.94).

Anal. Calc'd for $C_8H_{15}NO_3$: C, 55.57; H, 8.73; N, 8.14. Found: C, 55.5; H, 8.79; N, 8.53.

4,4-Dimethyl-5-nitro-2-hexanone was inert to both bromine and permanganate; it readily oxidized ferrous hydroxide. The infrared spectrum had medium intensity bands at 720 cm.$^{-1}$, 735 cm.$^{-1}$, 868 cm.$^{-1}$, 1165 cm.$^{-1}$, 1200 cm.$^{-1}$, and 1230 cm.$^{-1}$ A broad band of strong intensity was observed at 1300–1480 cm.$^{-1}$, and strong bands occurred

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(3) Kohler and Allen, *J. Am. Chem. Soc.*, **50**, 884 (1928).

(4) Kloetzel, *J. Am. Chem. Soc.*, **69**, 2271 (1947).

(5) Fishman and Zuffanti, *J. Am. Chem. Soc.*, **73**, 4466 (1951).

(6) Kohler and Barrett, *J. Am. Chem. Soc.*, **48**, 1770 (1926).

(7) King, *J. Am. Chem. Soc.*, **66**, 894 (1944).

also at 1540 cm.$^{-1}$, 1710 cm.$^{-1}$, and 2950 cm.$^{-1}$ The ultraviolet spectrum of a solution in 95% ethanol had a minimum at 253 mμ (log ε 1.94) and a maximum at 280 mμ (log ε 2.04). The oxime was a liquid, but a solid semicarbazone was obtained; this derivative melted at 165.5–166.0° (dec.) after two recrystallizations from aqueous methanol.

Anal. Calc'd for $C_9H_{18}N_4O_3$: C, 46.97; H, 7.87; N, 24.37. Found: C, 47.3; H, 8.00; N, 24.79.

Attention should be called to a severe explosion that occurred during distillation of the product from the attempted preparation of the nitrohexanone from methanolic mesityl oxide and nitroethane with a calcium hydride catalyst, using a reactant ratio of 1:10:1. The solid was filtered from the reaction mixture, washed with chloroform, and the filtrate then was distilled at atmospheric pressure to remove low-boiling material.[5] A white solid separated as the nitroethane fraction began to distill. A severe explosion then occurred, completely shattering the still. Traces of the white solid recovered afterwards were found to flash when heated momentarily in a flame. No such unstable materials were encountered when the reaction mixture was poured into aqueous hydrochloric acid and the organic material was removed by ether extraction.

5-Bromo-4,4-dimethyl-5-nitro-2-hexanone. A solution of bromine (90.95 g., 0.570 mole) in dry chloroform (200 cc.) was stirred and cooled (−50°) while solution of the sodium salt of the nitroketone in methanol (from 97.2 g., 0.561 mole, of nitro ketone and 0.561 mole sodium methoxide) was added over a 15 minute period; the temperature was maintained below −35°. Addition at below −10° over a period of 7 minutes did not appear to affect the yield. The mixture was stirred for one hour without cooling and then was mixed with water (300 cc.). The layers were separated and the aqueous layer was washed with three 50-cc. portions of chloroform. The combined chloroform solutions then were washed successively with water (two 20-cc. portions), aqueous sodium bisulfite (1.7%, two 60-cc. portions), and again with water (three 25-cc. portions), and dried ($MgSO_4$). Removal of the solvent left 141.5 g. (100% yield) of crude 5-bromo-4,4-dimethyl-5-nitro-2-hexanone. A sample was distilled twice and a center cut (n_D^{25} 1.4932) boiling at 94° (0.4 mm.) was submitted for analysis.

Anal. Calc'd for $C_8H_{14}BrNO_3$: C, 38.08; H, 5.60; N, 5.56. Found: C, 38.7; H, 5.68; N, 5.53.

1-Acetyl-2-nitro-2,3,3-trimethylcyclopropane (Ia). The crude bromonitro ketone (141.5 g., 0.561 mole) from the preceding experiment was mixed with a solution of freshly fused potassium acetate (220 g., 2.248 moles) in anhydrous methanol (800 cc.) and allowed to stand at room temperature for 10 hours. The solution then was refluxed for 8.5 hours, cooled, diluted with ether (500 cc.) to precipitate most of the salts, and then filtered. The precipitate was washed with ether, and the combined ether filtrates were concentrated to a volume of about 300 cc. Water (300 cc.) then was added, and the mixture was extracted with ether or benzene (four 100-cc. portions). The red extracts were combined, washed with water (four 60-cc. portions) and dried ($MgSO_4$). Solvent was removed and the residual oil was distilled through a 4-inch Vigreux column. After a forerun (4.07 g., n_D^{23} 1.4627), the pale yellow cyclopropyl ketone (70.17 g., 72.9%, n_D^{23} 1.4627) was collected at 73–83° (2.3–2.5 mm.). A 10-g. sample of the product was fractionated in a 60-cm. Piros-Glover spinning-band still in a search for the two stereoisomers of Ia. The whole sample distilled at 88.0° (4.25 mm.) at a 10:1 reflux ratio, and the three fractions collected all had the same refractive index (n_D^{25} 1.4619). The third fraction (2.42 g., d^{25} 1.0740 g./cc.; MR_D 43.81, exaltation = 3.40) was analyzed.

Anal. Calc'd for $C_8H_{13}NO_3$: C, 56.12; H, 7.66; N, 8.18. Found: C, 56.3; H, 7.95; N, 8.29.

1-Acetyl-2-nitro-2,3,3-trimethylcyclopropane (Ia) readily oxidized ferrous hydroxide but did not decolorize permanganate or bromine. It gave a positive iodoform test. A mixture of equal weights of Ia and phosphorus pentachloride, heated on a steam bath for 15 minutes, did not produce any chlorine. The infrared spectrum of Ia contained bands of medium intensity at 750 cm.$^{-1}$, 770 cm.$^{-1}$, 1030 cm.$^{-1}$, 1090 cm.$^{-1}$, 1260 cm.$^{-1}$, and 3000 cm.$^{-1}$ Strong absorption occurred at 850 cm.$^{-1}$, 880 cm.$^{-1}$, 965 cm.$^{-1}$, 1130 cm.$^{-1}$, 1180 cm.$^{-1}$, 1195 cm.$^{-1}$, 1320–1480 cm.$^{-1}$, 1550 cm.$^{-1}$, and 1715 cm.$^{-1}$ The ultraviolet spectrum of a solution of Ia in 95% ethanol showed no maxima or minima, but only gradually decreasing absorption between 220 mμ (log ε 3.55) and 330 mμ (log ε 1.66). However, the spectrum of an isooctane solution had maxima at 290 mμ (log ε 1.89) and 325 mμ (log ε 1.76) with minima at 270 mμ (log ε 1.87) and 310 mμ (log ε 1.61). The semicarbazone of Ia melted at 202–203° (dec.) after three recrystallizations from 95% ethanol.

Anal. Calc'd for $C_9H_{16}N_4O_3$: C, 47.37; H, 7.06; N, 24.56. Found: C, 47.6; H, 7.24; N, 25.52, 23.74.

The *2,4-dinitrophenylhydrazone of Ia*, after three recrystallizations from methanol, formed orange needles which melted at 163–166° (dec.). The analytical data suggested the presence of a molecule of methanol of crystallization.

Anal. Calc'd for $C_{15}H_{21}N_5O_7$: C, 47.00; H, 5.52; N, 18.28. Found: C, 47.3; H, 5.58; N, 18.24.

The *pyridinium iodide* prepared from Ia by King's method[7] was obtained in 73% yield. The salt melted at 183.5–184.0° (dec.) after two recrystallizations from methanol.

Anal. Calc'd for $C_{13}H_{17}IN_2O_3$: C, 41.50; H, 4.56; N, 7.45. Found: C, 42.0; H, 4.74; N, 7.25.

1-m-Nitrocinnamoyl-2-nitro-2,3,3-trimethylcyclopropane (IIa). Wallach's procedure[8] with a 90-minute reaction time at room temperature was used to prepare IIa from 1.71 g. (0.010 mole) of Ia. The ivory-colored product melted at 107.5–108° after four recrystallizations from a mixture of ethanol and ethyl acetate.

Anal. Calc'd for $C_{15}H_{16}N_2O_5$: C, 59.21; H, 5.30; N, 9.21. Found: C, 59.0, 60.0; H, 5.06, 5.47; N, 9.26.

1-(5-Phenyl-2,4-pentadienoyl)-2-nitro-2,3,3-trimethylcyclopropane (IIb). Wallach's procedure[8] was used, with 1.71 g. (0.010 mole) of Ia. The reaction mixture was allowed to stand at room temperature for 17 hours and then was refluxed for 3.5 hours. The crude product (2.82 g., 99%) was a viscous red oil that could be crystallized from methanol. The orange crystals (1.03 g., 36%) melted at 95–96.5°, and after two recrystallizations, at 96.2–97.0°.

Anal. Calc'd for $C_{17}H_{19}NO_3$: C, 71.54; H, 6.72; N, 4.92. Found: C, 71.5; H, 7.07; N, 4.92.

Reaction of 1-acetyl-2-nitro-2,3,3-trimethylcyclopropane with sodium methoxide. Both base-soluble and base-insoluble products were obtained when Ia was subjected to the action of sodium methoxide under a variety of conditions. However, several different unidentified solid products were isolated in small amounts from various experiments. The experimental conditions and the method of processing the product both appeared to influence the results. A typical experiment is described below.

A solution of the cyclopropane (Ia, 5.13 g., 0.030 mole) and sodium methoxide (from 2.07 g., 0.09 g.-atom, of sodium) in methanol (35 cc.) was heated at 55–65° for 2.5 hours. About 0.4 g. of sodium nitrite separated from the solution. The mixture was cooled, concentrated to about 20 cc. under reduced pressure, and poured into 50 cc. of water. The mixture was extracted with ether (four 20-cc. portions), and the ether extracts were washed with cold water (two 25-cc. portions) which had been saturated with carbon dioxide. The ether extracts were dried, and the ether was removed. About 2.0 g. of an oil remained. About half of this could be distilled at 65° (20 mm.) to 110° (0.4 mm.). The alkaline aqueous solution left from the ether extraction was neutralized with acetic acid (5.40 g., 0.01 mole) and then was extracted with ether (four 20-cc. portions). The ether

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[8] Wallach, *Chem. Zentr.*, *I*, 637 (1908).

extracts were washed with aqueous sodium bicarbonate (2¹/₂%, 20 cc.) and water (25 cc.). Removal of the ether left about 1.5 g. of a brown oil, a third of which was distillable at 19 mm. (b.p. about 140°); part of this distillate crystallized (m.p. 70–75°). Viscous gummy residues remained from both distillations.

The base-insoluble products from several experiments of this type were combined and distilled. The first fraction ($n_D^{26.5}$ 1.4642, b.p. 75–77° at 20 mm.) was unsaturated toward both bromine and permanganate and apparently was a mixture of nitrogen-containing and nitrogen-free ketones.

Anal. Calc'd for Ia ($C_8H_{13}NO_3$): C, 56.16; H, 7.66; N, 8.18. Calc'd for $C_8H_{12}O$: C, 77.38; H, 9.75. Found: C, 72.1; H, 9.65; N, 3.09.

This material formed a mixture of two 2,4-dinitrophenylhydrazones (m.p. 210–212° and 147.5–149.5°) which were separated by virtue of the much greater solubility of the lower-melting derivative in methanol. Several recrystallizations of the latter (red flakes from methanol) gave a product melting at 152.0–152.7° (dec.). The analytical data suggested that this was the 2,4-dinitrophenylhydrazone of $C_8H_{12}O$, which may be the acetyl analog of III.

Anal. Calc'd for $C_{14}H_{16}N_4O_4$: C, 55.25; H, 5.30; N, 18.42. Found: C, 55.46; H, 5.20; N, 18.63.

The solid isolated during distillation of the base-soluble reaction products melted at 81.0–82.2° after two sublimations at 0.15 mm. The white crystals decolorized both permanganate and bromine and were unstable, completely melting within two months. The instability and analytical value for nitrogen suggest that the solid may be 3,5-dimethylisoxazolone, the 5-methyl analog of IV.

Anal. Calc'd for $C_5H_7NO_2$: N, 12.38. Found: N, 11.7.

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An Empirical Method for Prediction of the Boiling Points of Halomethanes

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Received March 23, 1956

We have found that the boiling point of a halomethane may be estimated fairly reliably by adding to the boiling point of methane (−161.37°) certain parameters for each fluorine, chlorine, bromine, and iodine atom present and another parameter if the halomethane is a methyl halide, methylene dihalide, or haloform. Thus

$$\text{b.p. (°C.)} = -161.37 + n_FX_F + n_{Cl}X_{Cl} + n_{Br}X_{Br} + n_IX_I + X_{CH_n} \quad (1)$$

where n_F, n_{Cl}, n_{Br}, and n_I are the number of fluorine, chlorine, bromine and iodine atoms in the molecule, X_F, X_{Cl}, X_{Br}, and X_I are the parameters for the four halogens and X_{CH_3}, X_{CH_2} and X_{CH} are the parameters for mono-, di-, and tri-halomethanes, respectively.

Optimum values for the seven parameters were obtained from a least squares treatment using all of the reliable boiling point data available in the literature through September, 1955. Of the 69 possible halomethanes, boiling points for 52 have been reported. Five of these values were ignored since they were either determined at a pressure considerably below 760 mm. or were for compounds reported to boil with decomposition. The data on fluorodiiodomethane was also ignored for the reason to be described shortly. Of the remaining 46 boiling points (ranging from −128 to 190°) 16 appeared to have been determined with particular care, and were given double weight in the least squares treatment. These include all of the 14 compounds listed by Timmermans.[2]

The numerous arithmetic and algebraic operations involved in the summations over the 46 sets of data and solution of the resultant seven simultaneous equations in seven unknowns were accomplished by use of a high speed computer, Engineering Research Associates, model 1101. The values obtained for the parameters are listed below to the nearest hundredth of a degree.

$$X_F = 7.15,\ X_{Cl} = 59.06,\ X_{Br} = 87.15,\ X_I = 125.02,$$
$$X_{CH_3} = 77.68,\ X_{CH_2} = 85.99, \text{ and } X_{CH} = 46.79$$

It was then found that equation (1) and the parameters above gave estimated boiling points that differed from the 46 boiling points used by an average of 2.4° (standard deviation 3.4°) and from the 16 particularly reliable boiling points by an average of 1.7° (s. d. 2.0°). Only 4 of the 46 compounds deviated by more than 6.3°. These were CHF_3 and CH_2F_2 which boiled 10.9 and 9.5° higher than expected and CF_3Br and CF_3I which boiled 6.9° and 7.1° lower than expected. The deviations for CHF_3 and CH_2F_2 may be due to hydrogen bonding. Although better agreement could probably be obtained by use of an additional parameter for fluorine, this was not attempted.

Equation (1) predicts a boiling point of 142.6° for $CHFI_2$. The only boiling points recorded in the literature for this compound are 100.3°[3] and 50° at 50 mm.[4] The latter boiling point may be extrapolated to about 122° at 760 mm. Thomas, however, has reported that $CHFI_2$ boils at 78° at 65 mm. (equivalent to about 147° at 760 mm.).[5]

For the other 5 of our 52 compounds, boiling points were estimated by extrapolation to 760 mm. and were found to deviate from those predicted from equation (1) by an average 4.5°.

A referee has pointed out that the halogen parameters closely parallel the absolute boiling points of

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[1] Eastman Kodak Fellow, 1955–1956.

[2] Timmermans, *Physico-Chemical Constants of Pure Organic Compounds*, Elsevier Publishing Company, New York, N. Y., 1950, pp. 210–229.

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