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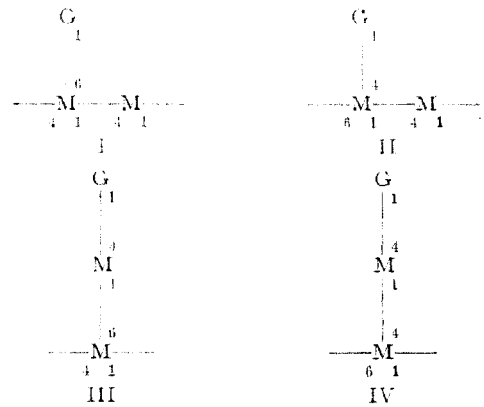
The Constitution of Guar Gum[1]

BY C. M. RAFIQUE AND F. SMITH

Guar gum extracted from the endosperm of guar seed is a galactomannan polysaccharide in which the ratio of D-mannose to D-galactose is 2:1.[2-5] The occurrence, properties and industrial uses of galactomannans of this type have already been described.[2-11]

This paper is concerned with the constitution of guar gum as revealed by methylation studies. The gum was methylated with methyl sulfate and sodium hydroxide and the separation and identification of the cleavage fragments of the methylated polysaccharide carried out by methods applied previously to the galactomannan of the carob bean.[12,13] Previous methylation studies have shown that 90% of the D-galactose component of the gum occupied terminal positions and that a dimethyl and a trimethyl derivative of mannose were also present in the mixture of cleavage fragments of the methylated polysaccharide.[14]

This work proves that these cleavage fragments consist of approximately equimolecular amounts of 2,3,4,6-tetramethyl-D-galactose, 2,3,6-trimethyl-D-mannose and 2,3-dimethyl-D-mannose. From this it can be deduced that the repeating unit of guar gum is to be represented by any one of the four formulas given below. The preliminary studies of Swanson enabled him to make the tentative suggestion that branched chain structures of this type might be present in the guar gum. All four formulas derive support from the evidence of periodate oxidation which demonstrates that the consumption of four moles of periodate is accompanied by the liberation of one mole of formic acid, a result which is at variance with that of previous workers.[6,8] There is, however, no unique solution to the structural problem although the possibilities may be reduced by recent X-ray evidence, published since this work was completed,



which appears to rule out the last two of the above four formulas and favors structure I.[15]

While there seems to be little doubt that the main structural features discussed above are correct, some additional evidence, as yet unexplained, has arisen from the preliminary results of paper partition chromatography[16] of the mixture of reducing methylated sugars derived from the methylated gum. This evidence shows that in addition to the three substances identified, namely, 2,3,4,6-tetramethyl-D-galactose, 2,3,6-trimethyl-D-mannose and 2,3-dimethyl-D-mannose, there are small amounts of two others which appear to be partially methylated derivatives of mannose. While the latter may arise as a result of incomplete methylation, it is of interest to note that they are still formed from methylated gum which has been subjected to permethylation with pyridinium methoiodide.[17] If methylation of the gum is complete and if the additional unidentified fragments do not result either from the scission of methoxyl groups[18] or from the condensation of hexose units to give oligosaccharides during methanolysis or hydrolysis, then the formation of these two additional products will have to be taken into account when the finer points of molecular structure of the gum come to be considered.

It is of interest to note that although the identification of the cleavage fragments of methylated polysaccharides is in most cases correctly based upon the isolation and characterization of crystalline derivatives, it is recognized that the yield of these derivatives is seldom, if ever, quantitative and that a mother liquor is not infrequently discarded. It seems not unlikely therefore that

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(13) F. Smith, THIS JOURNAL, **70**, 3249 (1948).

(14) J. Swanson, *ibid.*, **71**, 1510 (1949).

(15) K. J. Palmer and M. Ballantyne, *ibid.*, **72**, 736 (1950).

(16) *Cf.* E. L. Hirst, L. Hough and J. K. N. Jones, *J. Chem. Soc.*, 928 (1949).

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(18) K. Freudenberg and H. Boppel, *Ber.*, **73**, 609 (1940).

mother liquors, such as those encountered in this and other investigations connected with polysaccharides, may well contain compounds of important constitutional significance even though the amounts present are small. However, until the structure and origin of these small amounts of substances have been established, the above four formulas are tentatively advanced to represent the repeating unit of guar gum.

Experimental

The guar gum[19] used in these experiments was a grayish white powder which dissolved in water to give a neutral viscous solution which gave a complex with Fehling solution[20] but did not reduce it even on prolonged boiling. Dilute aqueous solutions of the gum formed a gel when treated with borax.[9,10] When a freshly prepared solution of the gum in water was centrifuged, an insoluble residue amounting to 9.5–11% of the original gum was obtained. This residue which gave positive tests for both proteins and carbohydrates slowly dissolved when kept in prolonged contact with water covered with a layer of toluene. When the insoluble fraction was heated for five hours at 95° with *N* sulfuric acid, a mixture of D-mannose and D-galactose was formed. These were identified by the isolation of methyl-α-D-mannopyranoside and mucic acid respectively.

Hydrolysis of the crude gum with *N* sulfuric acid in the above manner gave a mixture of D-galactose and D-mannose which showed a final value of $[\alpha]^{23}D$ +35° (*c*, 4.4) in the acid solution, a value which was found to be in close agreement with that shown by a solution of 2 parts of D-mannose and 1 part of D-galactose in *N* sulfuric acid. The syrupy mixture of reducing sugars isolated as above yielded D-mannose phenylhydrazone, m. p. and mixed m. p. 197°, and D-galactose-α-methyl-phenylhydrazone, m. p. and mixed m. p. 173°. Examination of the mixture of sugars on the paper chromatogram using butanol–ethanol–water as the developing solvent[21] confirmed previous findings[4] that D-galactose and D-mannose were the only reducing sugars present.

Fractionation of Guar Gum.—To a solution of the gum in water clarified by centrifugation, methanol was slowly added with stirring to give a series of fibrous precipitates which were washed with methanol, ether and dried *in vacuo* at 60°. The fractions showed $[\alpha]^{23}D$ +60°, +59° and +63°, respectively (*c*, 0.5 in 0.6 *N* NaOH) thus confirming the essential homogeneity of the soluble portion of the gum.[7] Paper partition chromatography of the mixture of sugars produced from these soluble fractions indicated that only D-galactose and D-mannose were present.

Oxidation of Guar Gum with Sodium Periodate.—To a solution of the purified gum (0.2505 g.) in water (150 ml.), 1.53 *N* sodium periodate (30 ml.) was added and the volume quickly adjusted to 250 ml. at room temperature. The mixture was cooled to 5° and kept at this temperature. At suitable intervals an aliquot was removed, treated with excess ethylene glycol, and the formic acid titrated with 0.01 *N* barium hydroxide using methyl red as the indicator.[22] The periodate consumption was determined at the same time on another sample by the usual arsenite method. After forty-eight hours, when the reaction was complete, 0.32 mole of formic acid was produced and 1.36 moles of periodate were consumed per anhydro-hexose unit. In two other experiments, the periodate consumption was 1.25 and 1.3 moles per anhydro-hexose unit (*cf.* refs. 6, 8).

Methylation of Guar Gum.—Since solutions of high concentrations of the gum either in sodium hydroxide or in water could not be stirred efficiently the methylation was conducted as follows. Methyl sulfate (300 ml.) and a solution of the gum (75 g.) in 30% sodium hydroxide (1000 ml.) were added with vigorous stirring to a solution of sodium hydroxide (50 ml.) at such a rate that the reaction mixture always contained an excess of sodium hydroxide. No external cooling was applied. After stirring for two hours the mixture was heated on a boiling water-bath for one hour, cooled, neutralized with dilute sulfuric acid and dialyzed overnight in cellophane bags to remove inorganic salts. Removal of the solvent by distillation *in vacuo* gave the partly methylated gum. Completion of the methylation and isolation of the methylated compound in the manner described in a previous paper[13] yielded a colorless or pale yellow tough glassy solid (yield 50 g.) $[\alpha]^{24}D$ +80.0° in acetone (*c*, 0.4) (found: OCH_3, 45.0). Fractional precipitation of the methyl gum from acetone solution with dry petroleum ether (b. p. 30–60°) in the usual way afforded seven fractions which differed very little from each other in specific rotation ($[\alpha]^{24}_{5461}$ +87° in acetone (*c*, 0.5)) and methoxyl content (45.9%).

Treatment of Methyl Guar Gum with Methyl Iodide in Pyridine.[17]—A specimen of the above methylated gum (1.0 g.) in anhydrous pyridine (50 ml.) was treated with methyl iodide (1.5 ml.) and heated for three hours at 150°. The excess of the pyridine was removed by distillation under reduced pressure and the residue subjected to dialysis for two days against distilled water. The methylated guar gum was recovered from the aqueous solution as described above (found: OCH_3, 44.8).

Methanolysis of Methylated Guar Gum.[13]—When the methylated gum (15.13 g.) was subjected to methanolysis, it reached a constant specific rotation of $[\alpha]^{23}_{5461}$ +91°. Fractional distillation of the mixture of glycosides thus produced gave: *Fraction I* (mainly methyl-2,3,4,6-tetramethyl-D-galactoside) (6.163 g.), b. p. bath temp. 116–120°, 0.06 mm., $n^{20}D$ 1.4498 (OCH_3, 59.3); *fraction II* (a mixture of methyl-2,3,4,6-tetramethyl-D-galactoside and methyl-2,3,6-trimethyl-D-mannoside) (0.818 g.), b. p. (bath temp.) 130°, 0.06 mm., $n^{20}D$ 1.4575, OCH_3, 54.0; *fraction III* (methyl-2,3,6-trimethyl-D-mannoside) (3.260 g.), b. p. (bath temp.) 130–135° (0.06 mm.), $n^{20}D$ 1.4610, OCH_3, 53.0; *fraction IV* (a mixture of methyl-2,3,6-trimethyl-D-mannoside and methyl-2,3-dimethyl-D-mannoside) (0.730 g.), b. p. (bath temp.) 145–155°, 0.06 mm., $n^{20}D$ 1.4708, OCH_3, 41.2; *fraction V* (methyl-2,3-dimethyl-D-mannoside) (4.011 g.), b. p. (bath temp.) 160°, 0.06 mm., $n^{20}D$ 1.4738, OCH_3, 40.2. There was an undistillable residue of 0.65 g. Redistillation of *fraction I* gave *fraction Ia* (5.443 g.) b. p. (bath temp.) 116–118°, 0.05 mm., $n^{20}D$ 1.4480, OCH_3, 59.8. The *residue Ib* (0.466 g.) had $n^{20}D$ 1.4572 and contained OCH_3, 54.8.

On the assumption that the refractive indices of methyl-tetra-, methyl-tri- and methyl-dimethyl-glycoside are $n^{20}D$ 1.4480, 1.4610 and 1.4738, respectively, the weight of methyl-tetramethyl-D-galactoside is 5.579 g. (1.2 mol. prop.) and the weights of methyl-2,3,6-trimethyl and methyl-2,3-dimethyl-D-mannoside are 4.375 g. (1.0 mol. prop.) and 4.570 g. (1.1 mol. prop.), respectively.

In two further experiments, portions of 8.0 g. and 20.0 g. of the methyl gum gave results which indicated that the molecular ratio of the methyl tetramethyl-D-galactoside, methyl-tri- and methyl-dimethyl-D-mannoside were 1.25:1.0:1.2 and 1.4:1.00:1.2, respectively. These results correspond to a composition of 35% D-galactose and 65% D-mannose approximately for guar gum (*cf.* ref. 2).

Identification of 2,3,4,6-Tetramethyl-D-galactose.—Hydrolysis of *fraction Ia* (1.72 g.) with 1 *N* sulfuric acid in the usual way gave 2,3,4,6-tetramethyl-α-D-galactopyranose (1.53 g.) b. p. (bath temp.) 130–135°, 0.1 mm., m. p. and mixed m. p. 70–72°, $[\alpha]^{24}D$ +162°, changing in forty-two hours to +138°, equilibrium value in water (*c*, 0.6); the rotation $[\alpha]^{24}D$ +102° changing to +83° is shown in ethanol and not in water as quoted erroneously by one of us (F. S.) in a previous paper.[13] *Anal.* Calcd. for $C_{10}H_{20}O_6$: OCH_3, 52.5; Found: OCH_3, 52.0.

(19) The authors wish to thank General Mills, Inc. (Minneapolis) for a generous supply of guar gum.

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Treatment of either the sirup recovered from the mother liquor or the crystalline material with boiling alcoholic aniline in the usual way afforded 2,3,4,6-tetramethyl-D-galactose anilide, m. p. and mixed m. p. 192°; $[\alpha]^{22}D$ −141° in pyridine (*c*, 0.8) (after crystallization from ethanol). *Anal.* Calcd. for $C_{10}H_{25}O_5N$: OCH_3, 40.0; Found: OCH_3, 40.2.

Identification of 2,3,6-Trimethyl-D-mannose.—Hydrolysis of fraction III (3.28 g.) with 2 *N* sulfuric acid at 95° gave 2,3,6-trimethyl-D-mannose as a liquid (2.8 g.), $[\alpha]^{22}D$ +15° in water (*c*, 1.0). *Anal.* Calcd. for $C_9H_{18}O_6$: OCH_3, 41.9; Found: OCH_3, 43.0. The 2,3,6-trimethyl-D-mannose gave the corresponding anilide which, however, proved difficult to purify. Oxidation of this trimethyl sugar with bromine afforded 2,3,6-trimethyl-D-manno-γ-lactone, m. p. and mixed m. p. 79°, $[\alpha]^{18}D$ +60.5° in water (*c*, 0.7).[12,13] *Anal.* Calcd. for $C_9H_{16}O_6$: OCH_3, 42.3; Found: OCH_3, 43.7.

The lactone yielded a phenylhydrazide which crystallized from ethanol as the monohydrate, m. p. 133° (*Anal.* Calcd. for $C_{15}H_{24}O_6N_2 \cdot H_2O$: C, 52.1; H, 7.6; N, 8.1; OCH_3, 26.9; H_2O, 5.2. Found: C, 52.15; H, 7.75; N, 8.3; OCH_3, 27.3; H_2O (loss in wt. at 100°) 5.4. After melting (preferably *in vacuo*) and cooling the anhydrous phenylhydrazide was obtained, m. p. 144° (before or after crystallization from absolute ethanol), $[\alpha]^{20}D$ −16.5° in water (*c*, 0.9). *Anal.* Calcd. for $C_{15}H_{24}O_6N_2$: OCH_3, 28.4; Found: OCH_3, 29.3 (*cf.* refs. 12, 13, 23).

Oxidation of the 2,3,6-trimethyl-D-mannose (1.75 g.) with nitric acid (d. 1.42) produced dimethoxyerythrosuccinic acid which upon esterification with ethereal diazomethane gave methyldimethoxyerythrosuccinate (methyl dimethyl-erythrarate) (0.90 g.) b. p. (bath temp.) 105–110°, 0.05 mm., $n^{26}D$ 1.4320–1.4330, m. p. and mixed m. p. 68° (after crystallization from ether). *Anal.* Calcd. for $C_8H_{14}O_6$: OCH_3, 60.2; Found: OCH_3, 60.0. The ester afforded the corresponding diamide, m. p. and mixed m. p. 257°.[24]

Identification of 2,3-Dimethyl-D-mannose.—One treatment of the methyl-dimethyl glycoside (*fraction V*) with sodium and methyl iodide in liquid ammonia[25] afforded methyl-2,3,4,6-tetramethyl-D-mannoside (found: OCH_3 60.1) which upon hydrolysis yielded 2,3,4,6-tetramethyl-D-mannose, identified as the anilide, m. p. and mixed m. p. 144°.

The methyl dimethylmannoside did not react with sodium periodate (0.05 *N*) at 5° even after six days.

Oxidation of the methyl dimethyl-D-mannoside (0.634 g. *fraction V*) with nitric acid and esterification of the acid so formed as described above for the methyl trimethyl-D-mannoside gave rise to methyl dimethoxyerythrosuccinate (0.35 g.) b. p. (bath temp.) 110°, 0.5 mm., $n^{28}D$ 1.4290–1.4295, m. p. and mixed m. p. 68°. A solution of the crystals in water (*c*, 0.65) was optically inactive. *Anal.* Calcd. for $C_8H_{14}O_6$: C, 46.6; H, 6.2; OCH_3, 60.2: Found: C, 46.7; H, 7.1; OCH_3, 60.1.

Hydrolysis of the glycoside (3.2 g. *fraction V*) with *N* sulfuric acid gave the corresponding 2,3-dimethyl-D-mannose (2.85 g.) $[\alpha]^{27}D$ +22° in water (*c*, 0.7). *Anal.* Calcd. for $C_8H_{16}O_6$: OCH_3, 29.8. Found: OCH_3, 29.7. This dimethyl-D-mannose (55 mg.) afforded an anilide which failed to crystallize. Two treatments of the sirupy dimethyl-D-mannose anilide with silver oxide and methyl iodide yielded the crystalline anilide of 2,3,4,6-tetramethyl-D-mannose, m. p. and mixed m. p., 143°.

Oxidation of the dimethyl-D-mannose (1.0 g.) with bromine in the usual way[12] afforded 2,3-dimethyl-D-mannono-γ-lactone (0.4 g.) as a viscous liquid $[\alpha]^{21}D$ +64.5° (initial value) in water (*c*, 0.7) changing in fifteen days to +35° (mutarotation incomplete). The lactone crystallized upon nucleation. *Anal.* Calcd. for $C_8H_{14}O_6$: OCH_3, 30.1; Found: OCH_3, 30.2. The lactone gave the phenylhydrazide of 2,3-dimethyl-D-mannonic acid, m. p. and mixed m. p. 156°, $[\alpha]^{22}D$ −24.2° in water (*c*, 1.7).[12,13]

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(24) F. Smith, *J. Chem. Soc.*, 571 (1944).
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Anal. Calcd. for $C_{14}H_{22}O_6N_2$: OCH_3, 21.4; Found: OCH_3, 21.5.

When a solution of the 2,3-dimethyl-D-mannose (0.884 g.) in 0.2 *N* periodic acid (120 ml.) was kept at 5° for fifty hours, 1.9 moles of periodic acid were consumed per mole of dimethyl sugar. The periodate and iodate ions were precipitated by the addition of barium hydroxide (0.4 *N*) and the solution, after filtration, concentrated *in vacuo* to about 20 ml. The distillate was treated with a slight excess of 5% alcoholic dimedone and the mixture concentrated under reduced pressure to about 25 ml.; this gave the dimedone derivative of formaldehyde m. p. and mixed m. p. 180° (yield 0.47 g. (after crystallization from water) corresponding to the formation of 0.37 mole of formaldehyde per mole of dimethyl sugar). Further experiments using sodium periodate as the oxidizing agent instead of periodic acid showed that approximately two moles of periodate were consumed for each mole of dimethyl sugar with the formation of 0.9 mole of formic acid. At the completion of these periodate oxidations optical activity was almost completely destroyed.

Investigation of the Composition of the Mixture of Reducing Methylated Sugars Produced from Methylated Guar Gum by Paper Partition Chromatography.—The mixture of methylated glycosides derived from the methylated gum was converted into the corresponding mixture of reducing methylated sugars by hydrolysis with *N* sulfuric acid in the usual way. Examination of this mixture of reducing methylated sugars by paper chromatography, using as the developing solvent the upper layer of a mixture of butanol (40 ml.), ethanol (10 ml.), ammonium hydroxide (1 ml.) and water (49 ml.)[16] furnished the results given in Table I. Two "spots" with R_G values of

TABLE I

R_G[b] VALUES OF SOME METHYLATED SUGARS

This table includes the R_G values of other methylated sugars besides those encountered in this work; these are included for reference purposes. The values differ slightly from those quoted by Hirst, *et al.*,[16] but this is probably due to a difference in temperature.

	Reducing methylated sugar	R_G values (25°C).
1	Mixture from methyl guar gum	0.22,[a] 0.39,[a] 0.63, 0.87, 0.93
2	2,3,4,6-Tetramethyl-D-galactose	0.93
3	2,3,4,6-Tetramethyl-D-mannose	1.0
4	2,3,6-Trimethyl-D-mannose	0.84
5	2,3,4-Trimethyl-D-mannose	0.86
6	2,3-Dimethyl-D-mannose	0.62
7	4-Methyl-D-mannose	0.40
8	2,3,4,6-Tetramethyl-D-glucose	1.0
9	2,3,6-Trimethyl-D-glucose	0.88
10	2,3-Dimethyl-D-glucose	0.68
11	3-Methyl-D-glucose	0.40

[a] These "spots" showed up only when the sirupy mixture of reducing methylated sugars was applied directly (without dilution) to the starting line of the chromatogram, thus indicating that they were present in small amounts. [b] R_G = (Distance travelled by the substance)/(distance travelled by 2,3,4,6-tetramethyl-D-glucose).

0.22 and 0.39 appeared on the chromatogram in addition to the three (R_G, 0.93, 0.87, 0.63) shown, respectively, by 2,3,4,6-tetramethyl-D-galactose, 2,3,6-trimethyl-D-mannose, and 2,3-dimethyl-D-mannose. Two unidentified "spots" were also shown by the mixture of reducing methylated sugars obtained from a specimen of methyl guar gum which had been methylated first by the methyl sulfate method and then by the pyridinium metho-iodide procedure[17] (see above). The unidentified "spots" also appeared in the chromatogram of the reducing methylated sugars obtained from the methyl-trimethyl-D-mannoside (*fraction III*) and the methyl-dimethyl-D-mannoside (*fraction IV*). Complete methylation of each of these

fractions followed by hydrolysis gave a product which showed a single "spot" on the chromatogram corresponding to 2,3,4,6-tetramethyl-D-mannose.

It is possible that the unidentified reducing sugars responsible for the "spots" on the chromatogram with R_G values of 0.22 and 0.39 are produced because the material is not completely methylated but if they are not due to incomplete methylation, the possibility must be borne in mind that the unidentified sugars are of constitutional significance. This problem will be the subject of further study.

Summary

Guar gum is a polysaccharide consisting of pyranose units of D-mannose (2 parts approx.) and D-galactose (1 part approx.) mutually joined by glycosidic bonds. Cleavage of the methylated gum yields approximately equimolecular amounts of 2,3,4,6-tetramethyl-D-galactose, 2,3,6-trimethyl-D-mannose, and 2,3-dimethyl-D-mannose. Each of these fragments has been characterized by the formation of crystalline derivatives. The gum molecule, built of a large number of repeating units containing one D-galactose and two D-mannose residues is highly branched and all side chains are terminated by a D-galactose residue. Four possible structures are postulated for the repeating unit of guar gum.

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Fluorinated Derivatives of Propane Containing a $-CHF_2$ Group

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This paper is presented as an extension of previously reported work on fluorine derivatives of propane.[1] Four compounds, each having the nucleus $-\overset{|}{\underset{|}{C}}-CCl_2-CHF_2$ were prepared starting from $CHCl{=}CCl-CHF_2$ (I). Chlorination of this olefin gave successively $CHCl_2-CCl_2-CHF_2$ (II) and $CCl_3-CCl_2-CHF_2$ (III) with no evidence of $CHCl_2-CCl_2-CF_2Cl$ (IV). The fluorination of (III) with antimony trifluoride and catalyst easily formed $CFCl_2-CCl_2-CHF_2$ (V) and $CF_2Cl-CCl_2-CHF_2$ (VI).

These compounds allow for interesting comparisons of the reactivity of the $-CHF_2$ and $-CHCl_2$ groups. In particular, compound (II), $CHCl_2-CCl_2-CHF_2$, since it contains both groups similarly situated, is well suited for such a comparison and has been subjected to two types of reactions: (a) photochlorination and (b) dehydrochlorination. As mentioned above, chlorination of (II) gave only (III) showing that the hydrogen of the $-CHF_2$ group is more resistant to displacement by chlorine than the hydrogen of the $-CHCl_2$ group. Dehydrohalogenation of (II) with alcoholic sodium hydroxide produced $CCl_2{=}CCl-CHF_2$ exclusively, indicating that the hydrogen of the $-CHF_2$ group is also more resistant to attack by alkali. The identity of the dehydrohalogenation product was established by its physical properties and by chlorination to (III).

Further evidence of the contrast in the reactivity of the hydrogen in the two groups is to be had from the following facts. The removal of hydrogen chloride from $CCl_3-CCl_2-CHCl_2$ is accomplished with great ease,[2] whereas the dehydrohalogenation of (III) to form $CCl_3-CCl{=}CF_2$ was not accomplished by the authors in spite of numerous attempts. The above examples lead to the conclusion that the hydrogen in the $-CHF$ group is unusually stable.

It is interesting that $CCl_3-CCl_2-CHF_2$ (m. p. 139.9°), although it contains the smaller fluorine atoms, melts 111° higher than $CCl_3-CCl_2-CHCl_2$.

The structure of (II) is assigned on the basis that it was made by chlorinating $CHCl{=}CCl-CHF_2$ and has the composition of a simple adduct. The structure of (III), m. p. 139.9°, is proved in that it was made by chlorination of (II), which could produce only two pentachlorides, one of which is known to be a liquid.[3]

It has been demonstrated that antimony trifluoride introduces fluorine into a $-CCl_3$ group in preference to a $-CCl_2-$ group[4] and that the boiling point is lowered approximately forty degrees for each chlorine–fluorine replacement in the $-CCl_3$ group.[5] Therefore the structures of compounds (V) and (VI) are assumed to be as given.

Experimental

Chlorine was added to 13.1 moles $CHCl{=}CCl-CHF_2$ (I)[1] (1930 g.) in sunlight until 13.1 moles (930 g.) was absorbed. Part of the material thus obtained was fractionated for pure $CHCl_2-CCl_2-CHF_2$ (II), b. p. 147.6°, $n^{20}D$ 1.4479, d^{20}_4 1.6582. Analysis for chlorine using a Stepanow reduction[6,7] followed by gravimetric determination of AgCl gave 65.20%; calculated, 65.10%.

Four moles (872 g.) of (II) was chlorinated further in sunlight until the gain in weight was about 100 g. The mixture, which had solidified during chlorination, was fractionated to give 430 g. boiling from 170–176°, which was essentially (III), b. p. 175.2°, m. p. 139.9° as determined from a freezing curve. *Anal.* Calcd. for $C_3HF_3Cl_5$: Cl, 70.26. Found: Cl, 70.45.

Fluorination of $CCl_3-CCl_2-CHF_2$ (III).—Antimony trifluoride, 0.34 mole (60.5 g.), and 0.675 mole of (III) (170 g.) was placed in a one-liter round-bottom flask and 0.167

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(2) Prins, *J. prakt. Chem.*, **89**, 414 (1914).

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