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.

ST. PAUL, MINNESOTA RECEIVED FEBRUARY 18, 1950

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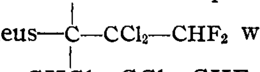
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF SOUTH CAROLINA]

# Fluorinated Derivatives of Propane Containing a $-CHF_2$ Group

BY H. W. DAVIS AND A. M. WHALEY

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 $C_3HF_2Cl_5$: 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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(1) Whaley and Davis, THIS JOURNAL, **70**, 1026 (1948).

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

(3) Henne and Ladd, THIS JOURNAL, **60**, 2491 (1938).

(4) Henne and Renoll, *ibid.*, **61**, 2489 (1939).

(5) Henne, "Organic Reactions," Vol. II, Roger Adams, Editor-in-Chief, John Wiley and Sons, Inc., New York, N. Y., 1944, p. 59.

(6) Stepanow, *Ber.*, **39**, 4056 (1906).

(7) Cook and Cook, *Ind. Eng. Chem., Anal. Ed.*, **5**, 186 (1933).

mole (50 g.) of antimony pentachloride added. There was attached to the reaction flask an eight-inch air reflux condenser which in turn was connected to an air condenser for distillation. On the application of heat the reaction proceeded smoothly and approximately one-half the product was distilled. Thereupon the reaction mixture was kept at reflux for thirty minutes and then the remainder of the product distilled after which it was washed with warm hydrochloric acid, then with water and dried over calcium chloride. Fractionation indicated 64 g. (VI), b. p. 92–92.5°, $n^{20}\text{D}$ 1.3787, $d^{20}_4$ 1.645 and 58 g. (V), b. p. 134.6°, m. p. 65.1° (from freezing curve). *Anal.* Calcd. for (VI), $C_3HF_4Cl_3$: Cl, 48.48. Found: Cl, 47.61. Calcd. for (V), $C_3HF_3Cl_4$: Cl, 60.13. Found: Cl, 60.44.

**Dehydrochlorination of $CHCl_2$-$CCl_2$-$CHF_2$ (II).**—In a two-liter three-neck flask, 2.35 moles (512 g.) of (II) was treated with 2.6 moles (104 g.) of sodium hydroxide dissolved in 780 ml. of methyl alcohol. The sodium hydroxide was dropped into the organic material with constant stirring, the temperature being kept at 25–30° by cooling with water as necessary. At the conclusion of the reaction the mixture was poured into water, the product was separated, dried and fractionated to give 345 g. of (VII), boiling from 113–114°. Passage of chlorine into this olefin in ultraviolet light produced (III).

**Acknowledgment.**—The authors are indebted to the Research Fund of the University of South Carolina for some financial assistance.

## Summary

The hydrogen in a $-CHF_2$ has been found to be more resistant to displacement by chlorine and attack by alkali than that in a $-CHCl_2$ group.

Four new compounds, $CHCl_2$–$CCl_2$–$CHF_2$, $CCl_3$–$CCl_2$–$CHF_2$, $CFCl_2$–$CCl_2$–$CHF_2$ and $CF_2Cl$–$CCl_2$–$CHF_2$ were prepared in the course of this investigation.

COLUMBIA, S. C. RECEIVED MARCH 13, 1950

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MARYLAND]

# Reaction Rates by Distillation. III. The Effect of Changes in Structure on the Rate of the Knoevenagel Reaction[1,2]

BY ERNEST F. PRATT AND ELEANOR WERBLE

An improved method of carrying out the Knoevenagel type of condensation, developed several years ago, involves continuous removal of the by-product water by distilling it into a phase separator.[3,4] Under the conditions used by previous investigators, however, the reaction mixture ordinarily was not homogeneous and the aqueous phase which appeared in the separator was not pure water so that no attempt was made to use the rate of appearance of the aqueous phase as anything more than an indication of the time necessary for complete reaction. The results described in previous papers of this series suggested that if certain modifications were introduced reactions of the type

$$p\text{-}RC_6H_4CHO + R'CH_2R'' \longrightarrow p\text{-}RC_6H_4CH{=}CR'R'' + H_2O$$

in which R′ and R″ are electron attracting groups, could be accurately followed by noting the rate of evolution of water. It seemed desirable to investigate the effects on the rate of variations in R, R′ and R″ since in spite of the wide application of condensations of this type little quantitative information on these fundamental points has heretofore been available. To our knowledge none of the condensations considered here have previously been carried out by the distillation method.

## Experimental[5,6]

**Purification of Materials.**—All starting materials were purified by the usual methods until their physical constants agreed closely with the values in the literature. These constants were as follows: benzene, $n^{25.5}\text{D}$ 1.4978; toluene, $n^{25.5}\text{D}$ 1.4935; caproic acid, $n^{20}\text{D}$ 1.4147; piperidine, $n^{20}\text{D}$ 1.4530; benzaldehyde, $n^{20}\text{D}$ 1.5450; anisaldehyde, $n^{28.5}\text{D}$ 1.5700; *p*-chlorobenzaldehyde, m. p. 46.5–47.5°; *p*-nitrobenzaldehyde,[7] m. p. 105–106°; 2-ethylhexanal, $n^{22.5}\text{D}$ 1.4154; diethyl malonate, $n^{20}\text{D}$ 1.4136; ethyl cyanoacetate, $n^{22.5}\text{D}$ 1.4165; ethyl acetoacetate, $n^{22.5}\text{D}$ 1.4188; phenylnitromethane,[8] $n^{21.8}\text{D}$ 1.5318; phenylacetone, $n^{21.7}\text{D}$ 1.5161; phenyl benzyl ketone,[9] m. p. 58.5–59.5°; malononitrile,[10] m. p. 30–32°; acetylacetone, $n^{24.2}\text{D}$ 1.4485; dibenzoylmethane, m. p. 78–79°; phenylacetonitrile, $n^{28.5}\text{D}$ 1.5189; ethyl phenylacetate, $n^{20}\text{D}$ 1.4985; phenyl benzyl sulfone,[11] m. p. 146–147°.

**Standard Procedure.**—The precautions previously described[12] were taken and the same apparatus and procedure were used except for the following modifications. One-eighth mole of active methylene compound and the desired amounts of piperidine and caproic acid were dissolved in sufficient benzene to fill a 250-ml. volumetric flask to the mark. A second 250-ml. volumetric flask was filled to the mark with benzene, a volume equal to the volume of aldehyde to be added was removed with a pipet and the remainder was mixed in the reaction flask with the solution of active methylene compound and catalyst. Because of its decreased volatility and water solubility the

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(1) From a portion of the Ph.D. thesis of Eleanor Werble, September, 1948.

(2) For the preceding article in this series, see Pratt, Preston and Draper, THIS JOURNAL, **72**, 1367 (1950).

(3) Cope, Hofmann, Wyckoff and Hardenbergh, *ibid.*, **63**, 3452 (1941), and earlier papers.

(4) Mowry, *ibid.*, **67**, 1050 (1945).

(5) Microanalyses by Mrs. Mary Aldridge. Values given are averages of duplicates.

(6) All melting points are corrected.

(7) Prepared by procedure of Leiberman and Connor, "Org. Syntheses," Coll. Vol. 2, p. 441 (1943).

(8) Prepared by procedure of Black and Babers, *ibid.*, p. 512.

(9) Prepared by procedure of Ballard and Dehn, THIS JOURNAL, **54**, 3970 (1932).

(10) Prepared by procedure of Corson, Scott and Vose, "Org. Syntheses," Coll. Vol. 2, p. 379 (1943).

(11) Prepared by procedure of Pummerer, *Ber.*, **43**, 1407 (1910).

(12) Pratt and Draper, THIS JOURNAL, **71**, 2846 (1949).