focussing camera (manufactured by Geo. C. Wyland; Ramsay, N. J.). Unfiltered chromium radiation was used. Two films, one having 15 lines and the other 17 were used. The observed values for each film were fitted by least squares to an equation of the form

$$\sin^2\theta = \lambda^2(h^2 + k^2)/4a^2 + \lambda^2 l^2/4c^2 + K\varphi\sin\varphi \quad (1)$$

where $\varphi = \pi - 2\theta$. The wave lengths for chromium radiation were taken as $K\alpha_1$, 2.28962; $K\alpha_2$, 2.29352; $K\beta_1$, 2.08479, all in units of 10^{-8} cm. The weighting procedure used, due to Hess[16] is a modification of that proposed by Cohen.[17] The essential change is that the points are weighted according to the error in the actual film measurements rather than by giving equal weight to each $\sin^2\theta$. The intensities of the observed lines are in qualitative agreement with those calculated from the assumed structure and value of u, but because of the possibility of preferred orientation in the back reflection camera we have not made quantitative estimates of intensities. The average deviation of $\sin^2\theta$ from that given by Eq. (1) was 0.00039.

The values of the parameters obtained from the least squares solution, taking both films into account, are $a = (4.8734 \pm 0.0005) \times 10^{-8}$ cm.; $c = (3.3103 \pm 0.0010) \times 10^{-8}$ cm. The ± represents the standard error. The values of a and c are for a temperature of 25°.

From the values of a and c and the molecular weight of 92.93 the calculated density is 3.925 ± 0.003 g. cm.$^{-3}$ at 25°. This is in good agreement with the measured density of 3.922 ± 0.004.

In the MnF_2 structure each manganese ion is surrounded by six fluoride ions. Using the observed parameters two of these are at a distance 2.14 Å. and four at 2.11 Å. The value of u necessary to make all six manganese–fluorine distances equal (2.120 Å.) is 0.3077. The six fluoride ions are arranged at the corners of a distorted octahedron. The two fluoride ions lying above (in the direction of the c-axis) or below the central manganese are closer to each other and farther from the remaining four than would be the case for a regular octahedron. The distance of these two closest fluoride ions is 2.62 Å. From Pauling's table of ionic radii[18] one computes a manganese–fluoride distance of 2.16 Å. and F–F distance of 2.72 Å. The observed distances are smaller than the radius sums as is found for other crystals with the rutile structure.[19]

Acknowledgment.—We are indebted to Mr. Larry Howell for performing the spectrochemical analysis and to Professor C. S. Barrett and Mr. J. B. Hess for assistance and advice regarding the X-ray measurements.

Summary

The preparation of single crystals of MnF_2 from the melt in an atmosphere of HF is described. From X-ray diffraction measurements the parameters of the tetragonal unit cell, each containing two molecules of MnF_2, are $a = (4.8734 \pm 0.0005) \times 10^{-8}$ cm. and $c = (3.3103 \pm 0.0010) \times 10^{-8}$ cm. at 25°. The parameter u that determines the position of the fluorine atoms in the space group D^{14}_{4h} is 0.310 ± 0.005. The density calculated from the X-ray parameters is 3.925 ± 0.003 g. cm.$^{-3}$. The measured density is 3.922 ± 0.004 at 25°. The melting point of MnF_2 is 929.5 ± 0.5°.

(16) J. B. Hess, *Acta Cryst.*, in press.

(17) M. U. Cohen, *Rev. Sci. Inst.*, **6**, 68 (1935); **7**, 155 (1936).

(18) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1940, p. 350.

(19) *Ibid.*, p. 365.

CHICAGO, ILLINOIS RECEIVED FEBRUARY 4, 1950

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

The Reaction of Chromyl Chloride with Olefins[1]

BY STANLEY J. CRISTOL AND KENDRICK R. EILAR

The first significant study of the action of chromyl chloride on organic compounds was made by Étard.[2] He discovered that chromyl chloride reacts with toluene to form a brown solid which when hydrolyzed produces benzaldehyde. This reaction, which now bears his name, has been extended to numerous nuclear-substituted toluenes.

Later, Étard reported[3] that an aldehyde was produced by the action of chromyl chloride on the olefin, camphene. Henderson and co-workers used this reaction to a considerable extent, but without great success, in their studies of the terpenes[4]; from reactions of chromyl chloride with several of the terpenes, they obtained mixtures of ketones, aldehydes, and chlorinated compounds; the constituents of these mixtures were usually not identified. Similar results were reported by Bredt.[5]

In view of the confusion arising from these terpene reactions,[6] it seemed desirable to study the

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(1) This paper was presented before the Division of Organic Chemistry at the March, 1949, meeting of the American Chemical Society, San Francisco, California.

(2) Étard, *Ann. chim. phys.*, **22**, 218 (1881).

(3) Étard and Moissan, *Compt. rend.*, **116**, 434 (1893).

(4) Henderson and Smith, *J. Chem. Soc.*, **55**, 45 (1889); Henderson and Gray, *ibid.*, **83**, 1299 (1903); Henderson and Heilbron, *ibid.*, **93**, 288 (1908); **99**, 1887 (1911); Henderson, Robertson and Brown, *ibid.*, **121**, 2717 (1922); Henderson and Chisholm, *ibid.*, **125**, 107 (1924).

(5) Bredt and Jagelki, *Ann.*, **310**, 112 (1899).

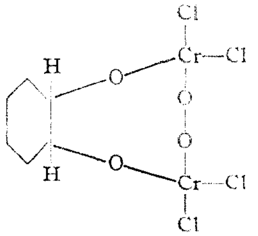
(6) Sword, *Chem. News*, **133**, 1 (1926).

reaction of some relatively simple olefins with chromyl chloride in carbon tetrachloride. It is the purpose of the present paper to report on the first results of this investigation.

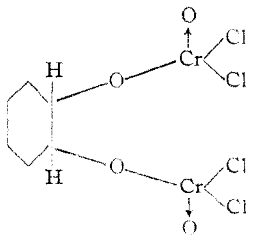
When cyclohexene was treated with chromyl chloride in carbon tetrachloride solution without any cooling other than the spontaneous refluxing of the solvent, two moles of chromyl chloride were used per mole of olefin before a permanent excess of chromyl chloride was produced. A brown solid similar to those obtained in the toluene and other oxidations was produced.[7] The solid was hydrolyzed and the organic product, which contained chlorine and gave only a trace test for aldehyde, was shown to be primarily *trans*-2-chlorocyclohexanol. Identification was made by physical properties and by the preparation of the α-naphthylurethan. The isolation of the chlorohydrin was somewhat unexpected in view of previous reports, but the results of the previous workers may be explained in terms of the known rearrangements of chlorohydrins to carbonyl compounds.[8,9]

The reaction between cyclohexene and chromyl chloride was vigorous and highly exothermic. When the reaction was conducted at 0°, only 1.5 moles of chromyl chloride was used per mole of olefin, and the yield of purified chlorohydrin was increased from 30 to 40%. When the reaction was conducted at −20°, only 1.2 moles of chromyl chloride were used per mole of olefin. In each of these reactions an excess of chromyl chloride was present at the end of the reaction, and the molar ratios of the reactants were determined by titration of the excess chromyl chloride after the solid was removed by filtration.

The solid formed in the reaction run at reflux temperature (in which two moles of chromyl chloride were used per mole of olefin) analyzed roughly for $C_6H_{10}(CrO_2Cl_2)_2$. The structure proposed by Sword[6] for this type of compound would be I, or, without the peroxide bond, II



I



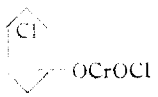
II

The hydrolysis of II (or I) would seem likely to lead to the formation of 1,2-cyclohexanediol as an intermediate, which in the aqueous solution would react with the hydrochloric acid formed in the hydrolysis to give the *trans* chlorohydrin.[10,11]

When the hydrolysis was carried out in aqueous sodium bicarbonate solution, the chlorohydrin was again obtained, no glycol being formed. This result, plus the fact that low temperature reactions gave solids with less than two moles of chromyl chloride per mole of olefin casts considerable doubt on the structures I or II for the brown solids. Unfortunately, we were unable to purify the solids to get good analyses, as no recrystallization solvent could be found and even warming in air often resulted in spontaneous ignition of the solid.

Titration of cyclohexene with a dilute standard solution of chromyl chloride in carbon tetrachloride gave the significant result that the first mole of reagent reacted rapidly with the olefin whereas the second mole reacted much more sluggishly. This was found to be typical of olefins, suggesting that the primary intermediate was $C_6H_{10}{\cdot}CrO_2Cl_2$ rather than $C_6H_{10}{\cdot}2CrO_2Cl_2$.[12]

These results suggest that the structure of the brown solid complex may be



III

which could easily hydrolyze to the *trans* chlorohydrin. The position of the excess chromyl chloride (above one mole) is not apparent. Evidence that it is not as in I or II comes from the fact that the hydrolysis gives little hexavalent chromium, suggesting that the excess has taken part in an oxidation–reduction reaction leading to destruction of the cyclohexane ring.[13]

A series of α-olefins was treated with chromyl chloride to determine the direction of addition. Chlorohydrins were formed in 35–50% yields from propylene, 1-butene, 1-pentene and 1-hexene, and in each case the hydroxyl group was located in the primary position as $RCHClCH_2OH$, opposite to that produced by the addition of hypochlorous acid to olefins.[14] Isobutylene produced only polymeric materials, as did styrene and stilbene.[15] In titration experiments using standard 1 *M* chromyl chloride as reagent, diisobutylene, α-pinene and α-methylstyrene reacted rapidly with one molar equivalent of chromyl chloride, and more slowly with the second mole at room temperature; *trans*-stilbene and phenanthrene reacted rapidly at room temperature with one mole

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[7] Previous workers[3-6] have all noted the formation of a brown precipitate comprising one mole of the hydrocarbon and two of chromyl chloride. These solids are insoluble in solvents with which they do not react and upon hydrolysis give organic materials and mixtures of tri- and hexa-valent chromium.

(8) Krassousky, *Bull. soc. chim.*, **30**, 213 (1903); *J. prakt. Chem.*, **75**, 241 (1907).

(9) Godchot, Mousseron and Granger, *Compt. rend.*, **200**, 748 (1935).

(10) Brønsted, Kilpatrick and Kilpatrick, THIS JOURNAL, **51**, 428 (1929).

(11) Michael, *Ber.*, **39**, 2785 (1906).

(12) Analysis of the brown solid arising from the reaction of an excess of cyclohexene with chromyl chloride in the cold gave results approximating the 1:1 compound.

(13) The complexes were observed to be paramagnetic; quantitative measurements were not conducted due to lack of purity.

(14) Saytzeff, *J. prakt. Chem.*, [2] **3**, 88 (1871).

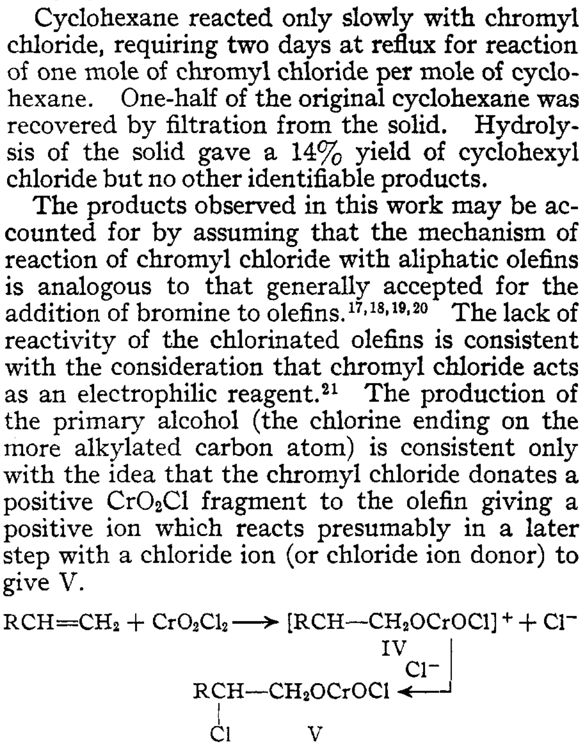
(15) We observed traces of benzaldehyde from these two olefins, as reported previously.[16]

(16) Henderson, *J. Chem. Soc.*, **85**, 1041 (1904).

of reagent and required heating for reaction of the second mole; methallyl chloride reacted with one mole rapidly in the cold, but did not react further. Neither trichloroethylene nor tetrachloroethylene reacted with chromyl chloride in refluxing carbon tetrachloride. The products of these reactions have not been studied.

Cyclohexane reacted only slowly with chromyl chloride, requiring two days at reflux for reaction of one mole of chromyl chloride per mole of cyclohexane. One-half of the original cyclohexane was recovered by filtration from the solid. Hydrolysis of the solid gave a 14% yield of cyclohexyl chloride but no other identifiable products.

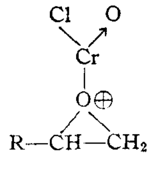
The products observed in this work may be accounted for by assuming that the mechanism of reaction of chromyl chloride with aliphatic olefins is analogous to that generally accepted for the addition of bromine to olefins.[17,18,19,20] The lack of reactivity of the chlorinated olefins is consistent with the consideration that chromyl chloride acts as an electrophilic reagent.[21] The production of the primary alcohol (the chlorine ending on the more alkylated carbon atom) is consistent only with the idea that the chromyl chloride donates a positive CrO_2Cl fragment to the olefin giving a positive ion which reacts presumably in a later step with a chloride ion (or chloride ion donor) to give V.



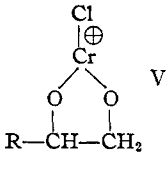
$$\mathrm{RCH{=}CH_2 + CrO_2Cl_2 \longrightarrow \underset{IV}{[RCH{-}CH_2OCrOCl]^+} + Cl^-}$$

$$\mathrm{\underset{V}{\underset{\displaystyle Cl}{RCH}{-}CH_2OCrOCl}} \xleftarrow{Cl^-} \mathrm{IV}$$

The positive ion intermediate IV may be a carbonium ion as written, but intermediates of this type are usually believed to exist as three-membered ring compounds, as in bromine addition[19] and various "neighboring-group" reactions[22] or as five-membered rings where the acetoxy group is vicinal,[22] in order to explain the steric course of addition or substitution reactions. Using these analogies, it seems better to write IV as VI or VII, the location of the charge on VII depending upon the resonance structure written.



VI



VII

Hydrolysis of V gives the chlorohydrin with appropriate positional and steric isomerism.

Experimental

The Reaction of Chromyl Chloride with Cyclohexene: *trans*-Cyclohexene Chlorohydrin.—A solution of 310 g. (2.0 moles) of chromyl chloride[23] in 150 ml. of carbon tetrachloride was added dropwise to a stirred solution of 82 g. (1.0 mole) of redistilled Eastman "White Label" cyclohexene in 200 ml. of carbon tetrachloride in a one-liter, three-neck, round-bottom flask fitted with a dropping funnel, reflux condenser, and stirrer. When the addition was complete, the contents of the flask were filtered, washed with fresh carbon tetrachloride, and dried with the aid of an aspirator and a rubber dam. The solid was then placed over paraffin and phosphorus pentoxide in a vacuum desiccator for twenty-four hours. The brown solid could not be further purified and was analyzed as such.

Anal. Calcd. for $C_6H_{10}(CrO_2Cl_2)_2$: Cr, 26.5; Cl, 36.2. Found: Cr, 24.2; Cl, 37.3.

The solid was then stirred portionwise into 400 ml. of cold water containing ice and sodium bisulfite, more ice and sodium bisulfite being added as necessary to keep the solution cold and to maintain an excess of reducing agent. After hydrolysis was complete, the lower organic layer was separated. The aqueous layer was extracted with two 200-ml. portions of ether. The ether extracts were combined with the organic liquid and dried over anhydrous sodium sulfate.

The ethereal solution was distilled under reduced pressure, and the distillate boiling at 85–105° (24 mm.) (57 g., 42%) redistilled under reduced pressure through a 14-inch Vigreux column. The product boiling at 90–92° (24 mm.) weighed 42 g. (31%) and had $n^{20}\mathrm{D}$ 1.4925; d^{25}_4 1.137; *M*D calcd., 34.08; found, 34.18. These values are consistent with those reported for 2-chlorocyclohexanol.[24,25] The material was shown to be the *trans* isomer by the preparation of the α-naphthylurethan derivative, m. p. and mixed m. p. with an authentic sample,[25] 165°.

In another preparation, the same general procedure was followed with the exception that only 155 g. (1.0 mole) of chromyl chloride was added, and the contents of the flask were kept at 0° by immersion of the flask in a salt-ice-bath. This procedure gave 54 g. (40%) of the chlorohydrin, $n^{20}\mathrm{D}$ 1.4924.

Another preparation carried out at 0 to −5° was similar with the exception that the contents of the flask were kept cold and stirred for three hours after the addition of the chromyl chloride solution was completed, and then the flask and contents were allowed to come to room temperature with continued stirring. The solid was removed by filtration, dried first with a rubber dam and then over paraffin and phosphorus pentoxide in a vacuum desiccator. This sample analyzed fairly well for a 1:1 adduct of olefin and chromyl chloride.

Anal. Calcd. for $C_6H_{10}CrO_2Cl_2$: Cl, 29.9. Found: Cl, 31.6.

When the brown solid was hydrolyzed in excess aqueous sodium bicarbonate, no water-soluble, steam-involatile organic fraction (cyclohexanediol) could be detected.

Reaction of Chromyl Chloride with Cyclohexane.—This reaction was carried out in a manner similar to that used in the reaction of cyclohexene, using one mole of each reactant, except that no solvent was used and the cyclohexane was heated to reflux during and after the addition of the chromyl chloride. Over one-half of the starting cyclohexane was recovered, and the only product isolated from the hydrolysis mixture was identified as cyclohexyl chloride (7 g.) by its properties[26]; b. p. 136–139° (630 mm.), $n^{20}\mathrm{D}$ 1.4616, d^{20}_4 1.0009.

2-Chloro-1-propanol.—Propylene[27] was led into a rapidly stirred solution of 155 g. (1.0 mole) of chromyl chloride in 300 ml. of carbon tetrachloride, the solution being

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(17) Ingold, *Chem. Revs.*, **15**, 225 (1934).

(18) Bartlett and Tarbell, THIS JOURNAL, **58**, 466 (1936).

(19) Roberts and Kimball, *ibid.*, **59**, 947 (1937).

(20) Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., New York, N. Y., 1940, pp. 147–150.

(21) Ingold and Ingold, *J. Chem. Soc.*, 2354 (1931); Anantakrishnan and Ingold, *ibid.*, 1396 (1935).

(22) Winstein and Buckles, THIS JOURNAL, **64**, 2780 (1942); *et seq.*

(23) Sisler, "Inorganic Syntheses," **2**, 205 (1939).

(24) Godchot and Bedos, *Bull. soc. chim.*, [4] **37**, 1454 (1925).

(25) Bartlett, THIS JOURNAL, **57**, 224 (1935).

(26) Sabatier and Mailhe, *Compt. rend.*, **137**, 241 (1903).

(27) Senderens, *ibid.*, **151**, 394 (1910).

kept cold by an ice-bath. When the color of chromyl chloride was discharged the flask had gained 23 g. in weight, corresponding to 0.55 mole of propylene absorbed. The solid was filtered, washed, and hydrolyzed in cold sodium bisulfite solution. The aqueous solution was saturated with salt, extracted with ether, and the latter solution dried over sodium sulfate. Distillation gave 22.4 g. (43%) of 2-chloro-1-propanol, b. p. 121–124° (613 mm.), $n^{20}\text{D}$ 1.4377, m. p. of 3,5-dinitrobenzoate 76.5–77.5°.[28] The melting point of the dinitrobenzoate was not depressed when mixed with that of an authentic sample of 2-chloro-1-propanol.[29] But when mixed with the 3,5-dinitrobenzoate (m. p. 76–76.5°) of 1-chloro-2-propanol,[30] the melting point was 59–65°.

2-Chloro-1-butanol.—Phillips "Pure Grade" 1-butene was treated with chromyl chloride in a manner similar to the reaction of propylene with chromyl chloride. The product boiling at 49–53° (13 mm.) amounted to 49% of theory, $n^{20}\text{D}$ 1.4428.[31] The 3,5-dinitrobenzoate, after four recrystallizations from aqueous alcohol, melted at 74–76°.

Anal. Calcd. for $C_{11}H_{11}O_6N_2Cl$: N, 9.26. Found: N, 9.22.

Five grams of the 2-chloro-1-butanol was warmed with concentrated nitric acid. After neutralization with sodium bicarbonate, acidification to a *p*H of 4 with sulfuric acid, extraction with ether and distillation, 1.5 g. of an acid was obtained, boiling at 189° (627 mm.). The acid contained chlorine and had a neutral equivalent of 122; the neutral equivalent calculated for α-chlorobutyric acid[32] is 122.5.

The acetate was prepared by refluxing 9 g. of 2-chloro-1-butanol with 20 g. of acetic anhydride for three hours. Water was added, and the immiscible acetate was separated, washed with sodium bicarbonate, dried over sodium sulfate, and distilled, giving 5.5 g. of the acetate, b. p. 158–162° (630 mm.); $n^{25}\text{D}$ 1.4255; d^{25}_4 1.0601; *M*D, calcd., 36.43; found, 36.36.

2-Chloro-1-pentanol.—By treating 1-pentene with chromyl chloride in a manner similar to those with propylene and 1-butene, a 43% yield of 2-chloro-1-pentanol was obtained, b. p. 59–64° (13 mm.), $n^{20}\text{D}$ 1.4457.

The 3,5-dinitrobenzoate was prepared; after three recrystallizations from 95% ethanol it melted at 69.5–71°.

Anal. Calcd. for $C_{12}H_{13}O_6N_2Cl$: N, 8.85. Found: N, 8.83.

Twenty-five grams of 2-chloro-1-pentanol was stirred with a solution of 180 g. of potassium dichromate in 150 ml. of concd. sulfuric acid and 500 ml. of water at room temperature for twelve hours. Extraction with ether and distillation gave 7.6 g. of α-chlorovaleric acid,[33] b. p. 111–121° (15 mm.); $n^{11}\text{D}$ 1.4497; $n^{23}\text{D}$ 1.4441; d^{23}_4 1.119; neut. equiv., calcd. 136.5, found, 141; *M*D calcd., 31.69, found, 32.43.

Anal. Calcd. for $C_5H_9O_2Cl$: Cl, 25.96. Found: Cl, 25.94.

2-Chloro-1-hexanol.—This compound was prepared from 1-hexene as above. Forty-two grams (36%) of product was obtained from 84 g. of 1-hexene, $n^{20}\text{D}$ 1.4486. Attempts to prepare the 3,5-dinitrobenzoate were unsuccessful. Oxidation by sulfuric acid–potassium dichromate mixture produced α-chlorocaproic acid,[34] b. p. 125° (15 mm.); $n^{23}\text{D}$ 1.4428; d^{23}_4 1.091; neut. equiv., calcd., 150.5; found, 154; *M*D, calcd., 36.31; found, 36.58.

Acknowledgment.—The authors are grateful to Julius Hyman and Company, Inc., Denver, Colorado, for generous financial support of this work.

Summary

A novel reaction has been found in which chromyl chloride reacts with olefins to give chlorohydrins. Cyclohexene has been converted to *trans*-2-chlorocyclohexanol in fair yields, and aliphatic olefins of the type RCH=CH₂ have been converted to β-chloro primary alcohols in 35–50% yields.

A possible mechanism is proposed for the reaction, consistent with the products observed and the relative reactivities of the olefins studied.

BOULDER, COLORADO RECEIVED MARCH 10, 1950

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(28) Gayler and Waddle, THIS JOURNAL, **63**, 3359 (1941).

(29) Dewael, *Bull. soc. chim. Belg.*, **33**, 504 (1924).

(30) Henry, *Ber.*, **7**, 414 (1874); *Rec. trav. chim.*, **22**, 324 (1903).

(31) Waddle and Adkins, THIS JOURNAL, **61**, 3361 (1939).

(32) De Boosere, *Bull. soc. chim. Belg.*, **32**, 44 (1923).

(33) Servais, *Rec. trav. chim.*, **20**, 45 (1901).

(34) Guest, THIS JOURNAL, **69**, 300 (1947).

[CONTRIBUTION NO. 765 FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PITTSBURGH]

The Partial Hydrogenation of Triolein

BY JAMES H. BENEDICT[1,2] AND B. F. DAUBERT

Introduction

Although it is known that the partial hydrogenation of oleic acid or its esters results in the formation of iso-oleic acids in addition to stearic acid, there is not complete agreement as to which isomers are produced. Moore[3] in 1919 partially hydrogenated ethyl oleate using palladium and nickel catalysts at 140 and 240°. Although he made no separation of his reaction products, Moore[3] concluded that the iso-oleic acids produced during these hydrogenations consisted of a mixture of 9-, 10- and 11-*trans*-octadecenoic acids.

Hilditch and Vidyarthi[4] hydrogenated methyl oleate using a nickel catalyst and then separated the solid fatty acids from the reaction products by the Twitchell lead salt procedure. On the basis of a potassium permanganate oxidation, they concluded that the hydrogenation produced 8-, 9- and 10-octadecenoic acids.

Since natural oils are composed of triglycerides it seemed desirable to study the course of the hydrogenation reaction for the simple triglyceride, triolein. While conducting this investigation a sample of triolein was hydrogenated in such a manner that a relatively large quantity of iso-oleic acids was produced.

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[1] Procter and Gamble Company Fellow.

[2] Procter and Gamble Company, Cincinnati 17, Ohio.

[3] C. W. Moore, *J. Soc. Chem. Ind.*, **38**, 320T (1919).

[4] T. P. Hilditch and N. L. Vidyarthi, *Proc. Roy. Soc. (London)*, **A122**, 552 (1929).