identity with bagasse native lignin is well founded. This identity may be further recognized in their infrared and ultraviolet absorption spectra.[4] In a forthcoming communication this conclusion will be further supported by means of oxidation studies with nitrobenzene and alkali and also by identifying their lignosulfonic acids.

Acknowledgments.—The bagasse used in these experiments was obtained through the courtesy of the Godchaux Sugars, Inc., New Orleans, La. The mold cultures used in this investigation were obtained through the courtesy of Dr. W. J. Robbins of the New York Botanical Garden. The analyses reported in this paper were carried out by Mr. A. A. Sirotenko of this Department. This work was carried out under the auspices of the Office of Naval Research.

NEW YORK, N. Y.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND THE DEFENSE RESEARCH LABORATORY, THE UNIVERSITY OF TEXAS]

Allylic Chlorides. XVIII. Preparation and Properties of 1,1,3-Trichloro-2-fluoro-1-propene and 1,1,2,3-Tetrachloro-1-propene[1]

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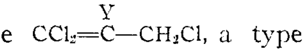
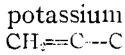
The following compounds have been prepared and characterized for the first time: 3-bromo-1,1-dichloro-2-fluoro-1-propene, 3,3-dichloro-2-fluoro-2-propen-1-ol, 1,1,3-trichloro-2-fluoro-1-propene, 2,3,3-trichloro-2-propen-1-ol and 1,1,2,3-tetrachloro-1-propene. The reactions of 1,1,3-trichloro-2-fluoro-1-propene and 1,1,2,3-tetrachloro-1-propene with potassium iodide and with sodium ethoxide have been studied.

The study of the influence of various groups and atoms on the reactivity of the allylic chlorine atom of substituted allyl chloride has been extended to include 1,1,3-trichloro-2-fluoro-1-propene and 1,1,2,3-tetrachloro-1-propene. Both of these compounds are of the type  $CCl_2{=}\overset{Y}{C}{-}CH_2Cl$, a type which shows a marked difference in its reaction with potassium iodide in acetone from the similar type  $CH_2{=}\underset{Y}{C}{-}CH_2Cl$.

The 1,1,3-trichloro-2-fluoro-1-propene was synthesized from 1,1-dichloro-2-fluoro-1-propene by the use of N-bromosuccinimide followed by hydrolysis of the 3-bromo-1,1-dichloro-2-fluoro-1-propene to 3,3-dichloro-2-fluoro-2-propen-1-ol and conversion of this allylic alcohol to the desired allylic chloride in a manner similar to that previously used to prepare the 1,3-dichloro-2-fluoropropenes from the 1-chloro-2-fluoro-1-propenes.[1] The 1,1,2,3-tetrachloro-1-propene was obtained by the dehydrochlorination of 1,1,2,2,3-pentachloropropane.

The pentachloropropane was prepared by the low temperature addition of chlorine to 1,2,3-trichloropropene.[3] Apparently no substitution occurred which conforms with the generalizations of Taft[4] on non-activated, low temperature chlorination reactions. The pentachloride obtained by the addition of chlorine to 1,2,3-trichloropropene is considered to be 1,1,2,2,3-pentachloropropane, although the physical constants of this compound do not agree very closely with those reported by Stevens,[5] which disagreement, however, is probably due in part to the higher purity of our sample.

The structure of 1,1,3-trichloro-2-fluoro-1-propene was related to 1,1-dichloro-2-fluoro-1-propene by replacement of the allylic chlorine atom by a hydrogen atom using lithium aluminum hydride.[6] The structure of 1,1,2,3-trichloro-1-propene was also confirmed in the same manner by its conversion to the known 1,1,2-trichloro-1-propene.[7]

The relative reactivities of 1,1,3-trichloro-2-fluoro-1-propene and 1,1,2,3-tetrachloro-1-propene with sodium ethoxide in ethanol (Table I) show the same relationship between the electron-attracting ability of the substituent on the number two carbon atom and reactivity as do those compounds having two hydrogen atoms on the number one carbon atom.[8] In both series the replacement of the hydrogen atom on the number two carbon atom by an electron attracting atom (Br, Cl or F) causes a decrease in reactivity. This similarity does not

TABLE I

RELATIVE REACTIVITY OF 1,1,3-TRICHLORO-2-FLUORO-1-PROPENE AND 1,1,2,3-TETRACHLORO-1-PROPENE WITH SODIUM ETHOXIDE IN ETHANOL AT 50°

1,1,3-Trichloro-2-fluoro-1-propene					
Time, hr.	6.50	8.50	10.5	12.5	22.0
Reacted, %	58.6	63.3	67.4	70.7	81.9
k, hr.$^{-1}$ mole^{-1} l.	4.37	3.88	3.87	3.81	3.83
Av. k			3.95±0.16		
Relative reactivity[a]			3.3		
1,1,2,3-Tetrachloro-1-propene					
Time, hr.	1.00	1.50	2.00	3.00	4.00
Reacted, %	36.1	43.5	50.7	60.7	67.9
k, hr.$^{-1}$ mole^{-1} l.	11.3	10.2	10.3	10.4	10.6
Av. k			10.6±0.3		
Relative reactivity[a]			9.0		

[a] Allyl chloride as 1.00 with k = 1.18.

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[1] For number XVII of this series see L. F. Hatch and D. W. McDonald, THIS JOURNAL, **74**, 2911 (1952).

[2] Research Corporation Fellow 1949–1950, Monsanto Fellow, 1950–1951.

[3] L. F. Hatch, J. J. D'Amico and E. V. Ruhnke, THIS JOURNAL, **74**, 123 (1952).

[4] R. W. Taft, *ibid.*, **70**, 3364 (1948).

[5] P. G. Stevens, *ibid.*, **68**, 620 (1946).

[6] L. F. Hatch and R. H. Perry, *ibid.*, **71**, 3262 (1949).

[7] G. Bersche and R. Fittig, *Ann.*, **133**, 117 (1865); W. Szenic and R. Taggesell, *Ber.*, **28**, 2668 (1895).

[8] L. F. Hatch and H. E. Alexander, THIS JOURNAL, **71**, 1037 (1949).

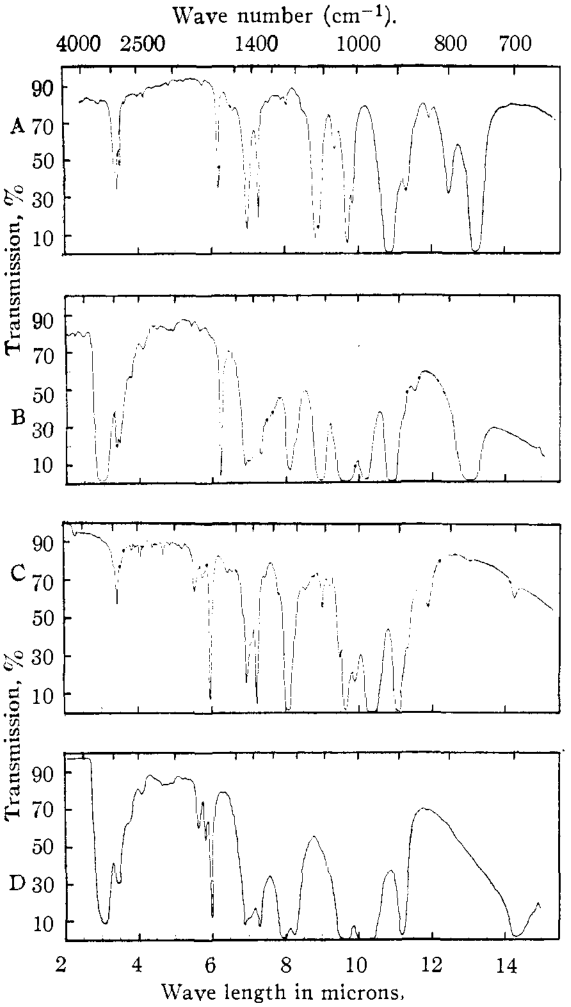

Fig. 1.—A, 1,1,2-trichloro-1-propene; B, 2,3,3-trichloro-2-propen-1-ol; C, 1,1-dichloro-2-fluoro-1-propene; D, 3,3-dichloro-2-fluoro-2-propen-1-ol.

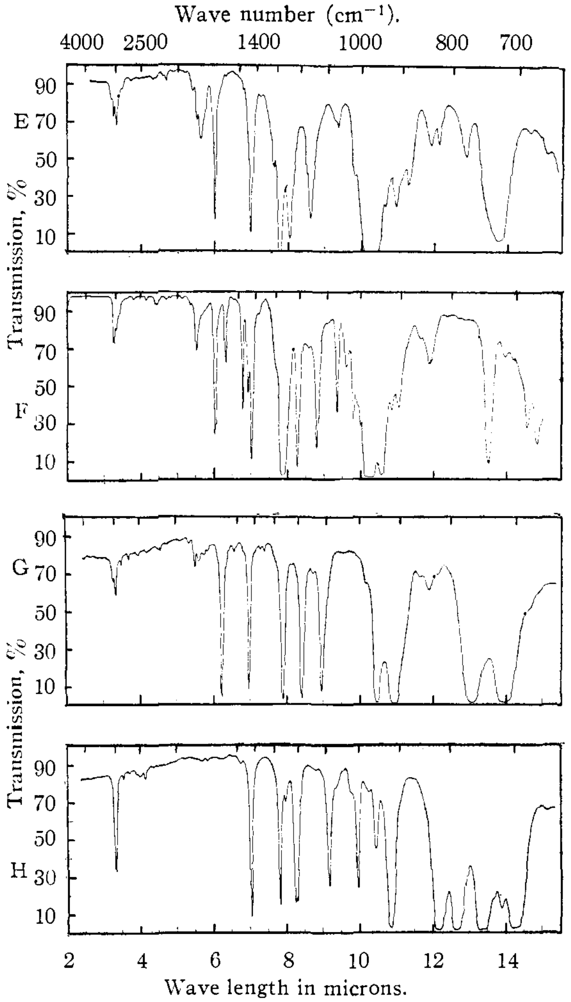

Fig. 1.—E, 1,1,3-trichloro-2-fluoro-1-propene; F, 3-bromo-1,1-dichloro-2-fluoro-1-propene; G, 1,1,2,3-tetrachloro-1-propene; H, 1,1,2,2,3-pentachloropropane.

hold, however, in respect to the electron releasing methyl group, for 1,1,3-trichloro-2-methylpropene has a relative reactivity (7.4)[8] which is between that of 1,1,2,3-tetrachloro-1-propene (9.0) and 1,1,3-trichloro-2-fluoro-1-propene (3.3). All three compounds are less reactive than 1,1,3-trichloro-1-propene (1.2)[9] while methallyl chloride (1.03) is slightly more reactive than allyl chloride (1.00).

The reactions of 1,1,3-trichloro-2-fluoro-1-propene and 1,1,2,3-tetrachloro-1-propene with potassium iodide in acetone were very rapid and were not second-order reactions. The possibility of this reaction involving an anionic attack on the vinyl $CCl_2=$ group followed by an allylic shift is being investigated. A similar mechanism has been proposed by Fainberg and Miller[10] to explain the rapid reaction between sodium iodide and $CF_2=CXCF_2$-Cl.

The atomic refraction of fluorine in the various compounds prepared during this investigation was 1.01 cc. per mole which is in close agreement with the value of 0.95 found for similar compounds previously prepared.[1]

Figure 1 gives the infrared spectra of the compounds prepared in this study. These spectra show no characteristics which are not in agreement with the assigned structures.

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Experimental

3-Bromo-1,1-dichloro-2-fluoro-1-propene.—1,1-Dichloro-2-fluoro-1-propene (Halogen Chemicals, Inc., Columbia, South Carolina) was dried and distilled through an 18-inch glass-helix packed column to give a product with the following constants: b.p. 77.7° (745 mm.); $n^{25}\text{D}$ 1.4196, $n^{30}\text{D}$ 1.4168; $d^{25}{}_4$ 1.3026, $d^{30}{}_4$ 1.2953 (lit.[11] b.p. 77°; $n^{20}\text{D}$ 1.4211).

A mixture of 1.42 moles of 1,1-dichloro-2-fluoro-1-propene, 1.00 mole of N-bromosuccinimide, 0.10 mole of benzoyl peroxide and 550 ml. of carbon tetrachloride was refluxed for 3.5 hours.[12] The product was worked up in the

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[9] Unpublished work of Stanley D. Zimmerman.

[10] A. H. Fainberg and W. T. Miller, Jr., Abstracts of the 119th American Chemical Society Meeting, April, 1951.

[11] Data Sheet, Halogen Chemicals, Inc., Columbia, South Carolina.

[12] K. Ziegler, A. Spath, E. Schaff, W. Shumann and E. Winklerman, *Ann.*, **551**, 80 (1942).

usual manner and distilled through the 18-inch column to give a 59% yield of 3-bromo-1,1-dichloro-2-fluoro-1-propene based on the N-bromosuccinimide: b.p. 52° (20 mm.); n^{25}_{D} 1.5130, n^{30}_{D} 1.5103; d^{25}_{4} 1.8069, d^{30}_{4} 1.7983.

3,3-Dichloro-2-fluoro-2-propen-1-ol.—The 3-bromo-1,1-dichloro-2-fluoro-1-propene (0.53 mole) was hydrolyzed to 3,3-dichloro-2-fluoro-2-propen-1-ol by the use of a 10% solution of sodium carbonate (1.06 moles) at 70° for five hours. The product was worked up in the usual manner and distilled through the 18-inch column. A 74% yield was obtained: b.p. 61° (10 mm.); n^{25}_{D} 1.4670, n^{30}_{D} 1.4650; d^{25}_{4} 1.5032, d^{30}_{4} 1.4970.

Anal.[13] Calcd.: Cl, 48.9. Found: Cl, 47.8.

1,1,3-Trichloro-2-fluoro-1-propene.—The 1,1,3-trichloro-2-fluoro-1-propene was prepared by the action of phosphorus trichloride (0.14 mole) on 3,3-dichloro-2-fluoro-2-propen-1-ol (0.35 mole) in pyridine (0.08 mole).[14] A 50% yield was obtained: b.p. 129° (747 mm.), 42.5° (35 mm.); n^{20}_{D} 1.4710, n^{25}_{D} 1.4689, d^{20}_{4} 1.5077, d^{25}_{4} 1.4999.

Anal.[13] Calcd.: Cl, 65.1. Found: Cl, 64.5, 64.7.

1,1-Dichloro-2-fluoro-1-propene.—The structure of the 1,1,3-trichloro-2-fluoro-1-propene (0.07 mole) was confirmed by the replacement of the allylic chlorine atom by hydrogen using lithium aluminum hydride (0.024 mole) in diethyl ether.[15] A 37% conversion with a 51% yield was obtained of 1,1-dichloro-2-fluoro-1-propene (b.p. 76.5–78°; n^{30}_{D} 1.4157).

1,1,2,2,3-Pentachloropropane.—The 1,1,2,2,3-pentachloropropane was prepared by the addition of chlorine to 1,2,3-trichloropropene[3] (1.59 moles) at 10° over a period of eight hours in the presence of light supplied by three 200-watt light bulbs placed adjacent to the reaction flask. Distillation of the reaction mixture through a three-foot glass-helix packed column gave a 74% yield of 1,1,2,2,3-pentachloropropane: b.p. 198° (742 mm.), 78–79° (16 mm.); n^{25}_{D} 1.5080, n^{30}_{D} 1.5053; d^{25}_{4} 1.6199, d^{30}_{4} 1.6130; lit.[5] b.p. 191–191.5° (755 mm.); n^{25}_{D} 1.5098; d^{25}_{4} 1.6326.

Anal.[13] Calcd.: Cl, 80.19. Found: Cl, 80.00, 80.06.

1,1,2,3-Tetrachloro-1-propene.—1,1,2,2,3-Pentachloropropane (1.09 moles) and ethanol (184 g.) were treated in a stirred one-liter flask with 1.09 moles of potassium hydroxide added portionwise over a period of six hours. After one hour of refluxing and two hours at room temperature, the reaction mixture was worked up in the usual manner and distilled through the 18-inch column to give a 64% yield of 1,1,2,3-tetrachloro-1-propene: b.p. 162° (743 mm.), b.p. 59° (17 mm.); n^{25}_{D} 1.5174, n^{30}_{D} 1.5150; d^{25}_{4} 1.5488, d^{30}_{4} 1.5424.

Anal.[13] Calcd.: Cl, 78.8. Found: Cl, 78.1.

2,3,3-Trichloro-2-propen-1-ol.—1,1,2,3-Tetrachloro-1-propene (0.25 mole) was stirred for 18 hours at 70° with 100% molar excess of sodium carbonate in a 10% solution. The reaction mixture was worked up in the usual manner and distillation through the 18-inch column gave a 51% yield of 2,3,3-trichloro-2-propen-1-ol: b.p. 199° (745 mm.), 88–89° (16–17 mm.); n^{25}_{D} 1.5193, n^{30}_{D} 1.5178; d^{25}_{4} 1.5553, d^{30}_{4} 1.5495.

Anal.[13] Calcd.: Cl, 66.3. Found: Cl, 66.1, 66.3.

1,1,2-Trichloro-1-propene.—1,1,2,3-Tetrachloro-1-propene (0.13 mole) was treated with 0.038 mole of lithium aluminum hydride in tetrahydrofuran for ten hours at reflux temperature. The reaction mixture was worked up in the usual manner and distilled through the 18-inch column. A 56% yield of 1,1,2-trichloro-1-propene was obtained with a 70% conversion: b.p. 114–115° (746 mm.); n^{25}_{D} 1.4798, n^{29}_{D} 1.4780; d^{29}_{29} 1.341; lit.[7] b.p. 115°, 116–117°; d^{14}_{14} 1.387.

Infrared Spectra.—The infrared spectra data were obtained through the courtesy of R. E. Kitson and the Chemical Division, Polychemicals Department, E. I. du Pont de Nemours and Company. The spectra were made in the liquid phase using a Perkin–Elmer Model 21 double beam spectrometer. Sodium chloride optics were used with a cell thickness of 0.035 mm. for 1,1-dichloro-2-fluoro-1-propene, 3-bromo-1,1-dichloro-2-fluoro-1-propene and 3,3-dichloro-2-fluoro-2-propen-1-ol, 0.037 mm. for 1,1,3-trichloro-2-fluoro-1-propene and 0.040 mm. for the other compounds.

Reaction with Potassium Iodide in Acetone at 20°.—The usual procedure was used[16]; however, the data obtained were not amenable to calculation on the basis of a second-order reaction. The 1,1,3-trichloro-2-fluoro-1-propene reacted to the extent of 53% in 0.25 hours, 72.4% in 1.50 hours and 72.8% in 3.00 hours, while 1,1,2,3-tetrachloro-1-propene reacted to the extent of 53.5% in 0.25 hours, 54% in 1.00 hours and 61.8% in 2.00 hours.

Reaction with Sodium Ethoxide in Ethanol at 50°.—The procedure used was the same as that previously described[5] and the data were calculated using the rate expression for a second order reaction. The sodium ethoxide solution was 0.05003 M for the reaction with 1,1,3-trichloro-2-fluoro-1-propene (0.05006 M) and 0.05005 M for the reaction with 1,1,2,3-tetrachloro-1-propene (0.05050 M). A plot of log $b(a - x)/a(b - x)$ *vs.* time gave a straight line for 1,1,3-trichloro-2-fluoro-1-propene between 46 and 82% reacted and between 35 and 68% reacted for the 1,1,2,3-tetrachloro-1-propene. 1,1-Dichloro-2-fluoro-1-propene reacted to the extent of 10% in 120 hours with sodium ethoxide in ethanol at 50°. No correction was made for this extent of reaction of the vinyl halides in calculating the reaction rate of allylic chlorine atom.

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[13] E. Chablay, *Ann. chim.*, **1**, 510 (1914).

[14] A. Juvala, *Ber.*, **63B**, 1989 (1930); L. F. Hatch and S. S. Nesbitt, THIS JOURNAL, **72**, 727 (1950).

[15] L. F. Hatch and R. H. Perry, *ibid.*, **71**, 3262 (1949).

[16] L. F. Hatch, L. B. Gordon and J. J. Russ, *ibid.*, **70**, 1093 (1948).