

**Ethyllithium and Thallous Chloride in the Presence of Ethyl Iodide, Ethyl Bromide and Ethyl Chloride.**—A suspension of 6.0 g. (0.025 mole) of thallous chloride in 25 ml. of ether containing 4.3 g. (0.028 mole) of ethyl iodide was cooled in an ice-salt-bath and stirred under nitrogen while 0.055 mole of ethyllithium in 75 ml. of ether was added during forty-five minutes. The resulting clear, colorless ether solution was treated with distilled water and there was obtained 9.7 g. (100% yield) of diethylthallium iodide.

The experiment was repeated except that 6.0 g. (0.055 mole) of ethyl bromide was used in place of the ethyl iodide, and the reaction was conducted at room temperature. Some black precipitate (metallic thallium) was formed during this reaction. It was separated by decanting the ether solution and washing with fresh ether. Treatment of the ether solution with water yielded 7.80 g. (91.3%) of diethylthallium bromide. The metallic thallium was converted to thallous iodide which weighed 0.80 g. representing 9.7% of the thallous chloride originally used.

The experiment was again repeated, but this time in place of the ethyl iodide gaseous ethyl chloride was bubbled into the mixture so that an excess was present throughout the course of the reaction. After four hours at room temperature there was obtained a 79% yield of diethylthallium chloride, subsequent to hydrolysis, and a 21.6% yield of metallic thallium, weighed as thallous iodide.

**Methylithium, Methyl Iodide and Lead Iodide.**—A suspension of 18.5 g. (0.04 mole) of lead iodide in 40 ml. of ether containing 10 g. (0.07 mole) of methyl iodide was stirred while a solution of 0.15 mole of methylithium in 100 ml. of ether was added during twenty minutes. The mixture gradually darkened and was quite black when about one-half of the methylithium had been added. The black color then rapidly disappeared and at the end of the reaction the ether solution was clear and colorless indicating a quantitative conversion of the lead iodide to tetramethyllead. The ether solution was washed with dilute hydrochloric acid and then with water after which it was dried over calcium chloride. This solution was placed in a Dewar flask and solid carbon dioxide was added until the temperature had been reduced to  $-60^{\circ}$ . With stirring a solution of 13.0 g. (0.08 mole) of bromine in 25 ml. of chloroform was added. The white precipitate of dimethyllead dibromide<sup>7</sup> was collected on a filter, washed with ether and ethyl acetate and air dried. The yield was 14.5 g. (92%).

*Anal.* Calcd. for  $C_2H_5Br_2Pb$ : Br, 40.2; Pb, 52.2. Found: Br, 39.4, 39.6; Pb, 52.6, 52.3.

**Methylmagnesium Halide, Methyl Iodide and Lead Halide.**—To a stirred suspension of 13.9 g. (0.05 mole) of

lead chloride in 25 ml. of ether containing 8 g. (0.055 mole) of methyl iodide was added during fifteen minutes 0.164 mole of methylmagnesium chloride in 100 ml. of ether. The resulting mixture was heated under reflux for one hour and then treated with cold dilute hydrochloric acid. There remained a little insoluble black precipitate (metallic lead) together with a little yellow precipitate (lead iodide). The ether solution was dried and treated with bromine to convert the tetramethyllead to dimethyllead dibromide. The yield was 14.0 g. (70%).

The experiment was repeated using methylmagnesium iodide, methyl iodide and lead iodide. There was obtained a 26.6% yield of metallic lead and a 66% yield of tetramethyllead (weighed as dimethyllead dibromide).

**Ethylmagnesium Bromide, Ethyl Iodide and Lead Halides.**—A solution of 0.14 mole of ethylmagnesium bromide in 100 ml. of ether was added during twenty minutes to a stirred suspension of 0.04 mole of lead chloride in 50 ml. of ether containing 0.064 mole of ethyl iodide. The mixture was then heated under reflux for three hours after which it was treated with dilute hydrochloric acid. There was obtained a 36% yield of metallic lead. The ether soluble lead compound was presumed to be tetraethyllead. It was not isolated.

The above experiment was repeated using lead iodide in place of lead chloride. There was obtained a 14.6% yield of metallic lead in the form of large crystals. The other 85.4% of the lead was presumably converted to ether soluble tetraethyllead. No attempt was made to isolate it.

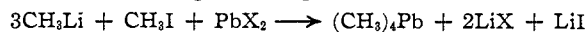
When the experiment was carried out using ethylmagnesium bromide, ethyl bromide and lead chloride 47% of the lead chloride was converted to metallic lead.

### Summary

The reaction of thallous halides with organolithium compounds in the presence of organic halides has been found to give high yields of  $R_3Tl$  compounds in accordance with the equation



Tetramethyllead has been prepared in excellent yields by the reaction of methylithium or methylmagnesium chloride and methyl iodide with lead halides according to the equation



There are indications that this type of reaction may be used to prepare other  $R_4Pb$  compounds.

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(7) Grüttner and Krause, *Ber.*, **49**, 1415 (1916).

[CONTRIBUTION FROM THE FLUORINE LABORATORIES OF THE PENNSYLVANIA STATE COLLEGE]

## Fluorocarbon Chemistry. III. Hydrogenolysis of Carbon-Carbon Bonds of Fluorocarbons<sup>1</sup>

BY W. R. JAMES,<sup>2</sup> W. H. PEARLSON<sup>3</sup> AND J. H. SIMONS

The thermal halogenolysis of carbon-carbon bonds of fluorocarbons with the resultant formation of fluorocarbon halides of shorter chain length has been reported in a previous paper.<sup>1</sup> The general reaction of carbon-carbon bond splitting in fluorocarbons is here extended to include the process of hydrogenolysis. The principal prod-

(1) For Paper No. II of this series see T. J. Erice, W. H. Pearlson and J. H. Simons, *THIS JOURNAL*, **71**, 2499 (1949).

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ucts isolated, shorter chain fluorocarbon derivatives containing one or two hydrogen atoms per molecule, were those to be expected from splitting of carbon-carbon bonds. Reactions involving carbon-fluorine bonds apparently resulted chiefly in complete decomposition of the molecule.

A previously reported catalytic reaction of hydrogen with fluorocarbons resulted in replacement of fluorine by hydrogen without indications of chain breaking.<sup>4</sup>

As in the halogenolysis experiments, the re-

(4) A. V. Grosse and G. H. Cady, *Ind. Eng. Chem.*, **39**, 367 (1947).

actions are carried out at high temperatures, *ca.* 700–900°, using relatively inert reactor tubes and a continuous flow process. This process involves, in general, passing a mixture of hydrogen and fluorocarbon vapor through an electrically-heated inert reactor, removing acid gases, then separating and identifying the products. Metal reactors, such as steel or Monel pipe, gave extensive decomposition and were replaced by carbon and graphite-lined tubes.

Considerable difficulty was encountered in separating the hydrogen-containing products from the fluorocarbons. The one and two carbon hydrogen-containing fluorocarbons such as  $\text{CF}_3\text{H}$ ,  $\text{CF}_2\text{H}_2$  and  $\text{C}_2\text{F}_5\text{H}$  are not completely miscible with fluorocarbons at low temperatures, so that fractional distillation had to be supplemented by mechanical separation of two-phase systems at low temperatures and conversion of the hydrogen compounds to chlorides or bromides. Preferential photochemical chlorination was used to separate other hydrogen-containing compounds from fluoroform, which can be chlorinated photochemically only under drastic conditions.<sup>5</sup>

### Experimental

**Reaction Tubes.**—A number of experiments were made initially using steel and Monel reactors; so much decomposition to carbon and hydrogen fluoride was observed that the use of these reactors was abandoned. Carbon and graphite-lined reactors were more satisfactory. For convenience in handling, they were put in tight-fitting metal tubes. The graphite tube, 16"  $\times$  3/4" i. d., was machined down to fit inside a Monel tube, 16"  $\times$  1" o. d.  $\times$  0.032"; the carbon tube, 13"  $\times$  3/4" i. d., was similarly fitted into a nickel tube of the same dimensions as the Monel tube. Organic fillers in the tubes were removed by prolonged heating at 790–850° in a stream of dry nitrogen. As a check on the completeness of this process, the nitrogen emerging from the tube was passed through a trap cooled in liquid air; the tube was considered free of volatile filler when nothing was condensed in the trap over a period of several hours.

The graphite-Monel and carbon-nickel tubes were used as liners for the reactor tubes; these reactors were 24" lengths of 1" steel pipe. The annular space between the nickel (or Monel) and the iron pipe was closed with silver wire wound on the tube. In a number of experiments nickel or copper thermocouple wells inside the carbon liners and extending to the reaction zone were used. In other experiments the metal wells were not used and temperatures were measured either by a thermocouple outside of the steel pipe or by calibrating the furnace temperature (with the reactor in it) in terms of the current through the furnace heating coils. The latter procedures are preferable since some decomposition occurred on the metal thermocouple wells.

**Fractionating Columns.**—Several columns were used. A small portable low-temperature column of the type described by Ramler and Simons<sup>6</sup> was used. For more precise work two low temperature columns connected to the vacuum system and operated in conjunction with a gas density balance were employed. Column No. 1 had a 45 cm. section of 11 mm. tubing packed with 1/16" glass or 1/16" stainless steel single-turn helices. Column No. 4 had a 55-cm. section of 17-mm. tubing packed with 1/16" glass helices. A conventional total condensation-partial take-

off column was used for distillations above room temperature; it had a 32 cm. section of 11 mm. tubing packed with 3/64" stainless steel helices.

**General Procedure.**—Gaseous fluorocarbons were taken from cylinders or evaporated from weighed ampoules; rates of flow were measured by an orifice-type flowmeter. Tank hydrogen was metered through a second flowmeter and mixed with the fluorocarbon just before passage through the reactor. Liquid fluorocarbons were introduced by bubbling the hydrogen stream through the hot fluorocarbon contained in a bubbler and passing the resultant mixture into the reactor. The gases from the reactor were passed through a sodium fluoride tube and then condensed in a liquid air-cooled trap. Treatment of the products varied, but the usual procedure was to pass the products through a potassium hydroxide scrubber followed by a phosphorus pentoxide-packed tube. The dry, air-free material was then introduced into the vacuum system for fractionation and other treatment.

**Hydrogenolysis of  $\text{C}_3\text{F}_8$ .**—Only the experiments carried out in the carbon and graphite-lined reactors are described. The  $\text{C}_3\text{F}_8$  used was part of the material obtained by the operation of the electrochemical process using butyric acid.<sup>7</sup> It had a molecular weight of 186 and a boiling range of -38 to -35°.

Three experiments are included; in two of these the nickel thermocouple well was present while in the third the well was absent. Conditions of temperature and flow rate were nearly the same for all three experiments. The products of the three experiments were fractionated separately and similar fractions combined for further investigation. For simplicity the three experiments are described collectively.

A total of 440 g. (2.3 moles) of  $\text{C}_3\text{F}_8$  was passed through the reactors at 775–840° using a hydrogen:fluorocarbon mole ratio of 2:1 and a fluorocarbon flow rate of 0.13 mole per hour. The total product collected amounted to 371.5 g. After passage through dilute potassium hydroxide, 360 g. remained. The carbon formed weighed 5.5 g., corresponding to 27.5 g. of fluorocarbon.

The products were dried, freed from permanent gases, and introduced into the vacuum system. After being condensed in a bulb made of 21-mm. Pyrex tubing connected to the manifold of the vacuum system through a stopcock, the liquid layers were allowed to separate. The lower layer and part of the upper layer were then frozen in liquid air, while the exposed portion of the upper layer was slowly evaporated out of the bulb and condensed in another part of the system. Evaporation was continued until only 1/2" of the upper layer remained. The residual upper layer and part of the lower layer were stripped off, condensed in a second bulb of 10 mm. tubing, and the process repeated. It was necessary only to obtain enough separation that the individual portions would be homogeneous during distillation. The upper and lower layers were then fractionated separately into a few fractions with broad boiling ranges.

TABLE I

FRACTIONATION OF HYDROGENOLYSIS PRODUCTS OF $\text{C}_3\text{F}_8$			
Fraction	Boiling range, °C.	Mol. wt.	Wt., g.
Upper layers			
I	-102 to -85	43 to 67	10.5
II	-85 to -80	69 to 70.5	56.5
III	-80 to -54	63 to 87	11.5
IV	-54 to -47	103 to 108	24
Lower layers			
V	-77 to -51	80 to 119	9
VI	-51 to -41	129 to 154	16
VII	> -41	184–189	212.5

(5) A. L. Henne, *THIS JOURNAL*, **59**, 1200 (1937).

(6) E. O. Ramler and J. H. Simons, *Ind. Eng. Chem., Anal. Ed.*, **14**, 30 (1942).

(7) J. H. Simons, *et al.*, presented before the Division of Physical and Inorganic Chemistry of the American Chemical Society, Portland, Oregon, September 1948; *J. Electrochem. Soc.*, **95**, 47 (1949).

Fractions I, total weight 10.5 g., were combined and the lower boiling material separated roughly from the  $\text{CF}_3\text{H}$ . Photochemical chlorination of the low boiling fraction (4.5 g.) yielded 7 g. of high boiling polychlorides and 3 g. of unreacted  $\text{CF}_3\text{H}$ ; total  $\text{CF}_3\text{H}$  from these fractions I, 9 g. The polychlorides contained a solid identified as  $\text{C}_2\text{Cl}_6$ ; m. p., 182–183° (sealed tube), no depression on mixed m. p. with an authentic sample of  $\text{C}_2\text{Cl}_6$ .

Fractions II, 56.5 g., were  $\text{CF}_3\text{H}$ . Calcd. mol. wt. 70, lit. b. p. -84.4° (-82.2°).<sup>8</sup>

Fractions III, 11.5 g., all proved to be two-phase systems when liquefied. They were combined and the phases separated by the previously described method. The lower layer, ca. 5 g., was largely (3.5 g.)  $\text{C}_3\text{F}_8$ , mol. wt. 183–187. The upper layer, 8 g., had a mol. wt. range of 60.7 to 61.6. It was chlorinated photochemically in a 12-liter Pyrex bulb. The lowest boiling material left was apparently  $\text{CF}_2\text{H}$ ; wt. 4 g., mol. wt. 73.5 to 74, b. p. ca. Dry Ice temperature.  $\text{CF}_3\text{H}$  is known to be unaffected by chlorination under the conditions used. The next higher boiling material, 6 g., was fractionated in the portable column and 2 g. of  $\text{CF}_2\text{Cl}_2$  was isolated; b. p., -33 to -31°, mol. wt., 124–124.5. Calcd. for  $\text{CF}_2\text{Cl}_2$ , 121, lit. b. p., -30°. Both  $\text{C}_2\text{F}_5\text{H}$  and  $\text{CF}_2\text{H}_2$  were found to chlorinate photochemically to give  $\text{C}_2\text{F}_5\text{Cl}$  and  $\text{CF}_2\text{Cl}_2$ . There also remained a residue of material boiling up to 135°, probably polychlorides.

Fractions IV and VI were thought to be mainly  $\text{C}_2\text{F}_5\text{H}$ , with smaller amounts of  $\text{CF}_2\text{H}_2$  and  $\text{C}_3\text{F}_8$ . The combined fractions, 40 g., did not separate into two phases when cooled. Careful fractionation in column No. 1 gave as the major fraction 20 g. of material of b. p. -50 to -49°, mol. wts., 122–129–123; calcd. for  $\text{C}_2\text{H}_5\text{H}$ , 120; lit. b. p., -48.5°. The variation of mol. wt. indicates contamination, probably by  $\text{C}_3\text{F}_8$ . The column residue had a low mol. wt. of 105. Redistillation of IV and VI gave the same results.

A 15-g. portion of the -49 to -48° fraction and the two fractions boiling at -58 to -48 to -31°, 8 g. and 3 g., were combined and brominated thermally. Part of the material was accidentally lost, but fractionation of the recovered bromination products yielded 15 g. of  $\text{C}_2\text{F}_5\text{Br}$ ; b. p., -24 to -20°, mol. wt. 195–200; calcd. mol. wt., 199; lit. b. p. -23 to -21°. The identification of fractions IV and VI as principally  $\text{C}_2\text{F}_5\text{H}$  was thus accomplished.

Fractions V were considered, because of their boiling ranges and molecular weights, to be primarily  $\text{C}_2\text{F}_5\text{H}$  and  $\text{CF}_3\text{H}$ .

Fractions VII were considered to be recovered  $\text{C}_3\text{F}_8$ .

From the composition of the individual fractions, the estimated amounts of each product were calculated.

TABLE II

SUMMARY OF THE PRODUCTS OF THE HYDROGENOLYSIS OF  $\text{C}_3\text{H}_8$ 

Compound	Wt., g.
$\text{CF}_3\text{H}$	73.0
$\text{C}_2\text{F}_5\text{H}$	34.5
$\text{CF}_2\text{H}_2$	Traces
Carbon	5.5

Of the  $\text{C}_3\text{F}_8$  introduced, about 27% was converted to recovered products, 6% to carbon (total decomposition) and 52% was recovered unchanged. Approximately 85% of the  $\text{C}_3\text{F}_8$  is thus accounted for.

**Hydrogenolysis of  $\text{C}_4\text{F}_{10}$ .**—The  $\text{C}_4\text{F}_{10}$  used was obtained by fractionation of the products of the operation of the

(8) O. Ruff, O. Bretschneider, W. Luchsinger and G. Miltschitzky, *Ber.*, **69**, 299 (1936); A. L. Henne, *This Journal*, **69**, 1200 (1937).

(9) T. Midgley and A. L. Henne, *Ind. Eng. Chem.*, **22**, 542 (1930).

(10) D. S. Young, N. Fukuhara and L. A. Bigelow, *This Journal*, **62**, 1171 (1940).

(11) T. J. Brice, W. H. Pearlson and J. H. Simons, *ibid.*, **68**, 968 (1946).

electrochemical process using adipic acid; b. p. -3 to +1°, mol. wt. 234–238. Two experiments were made, one at 705–740° in graphite with a copper thermocouple well in the reaction zone and one at 840–850° without the well. At 805° without the copper well the reaction was relatively slow.

In the 705–740° experiment, 201 g. (0.85 mole) of  $\text{C}_4\text{F}_{10}$  mixed with excess hydrogen in a mole ratio of 2.5:1 was passed through the reactor at a flow rate of 0.12 mole of fluorocarbon per hour. The products collected amounted to 178 g.; the carbon formed was 1.5 g., corresponding to ca. 7.5 g. of fluorocarbon. The products were separated roughly in the portable column into fractions boiling below and above -6°. The material boiling above -6°, considered to be  $\text{C}_4\text{F}_{10}$ , amounted to 117 g.

The lower boiling fraction was found to consist of two liquid phases which were separated as in the  $\text{C}_3\text{F}_8$  experiments, passed through dilute base, dried over phosphorus pentoxide and fractionated separately in column No. 1.

Fractionation of the upper layer, 32.5 g., yielded 0.13 mole (9 g.) of  $\text{CF}_3\text{H}$  (b. p. -81 to -78°, mol. wt. 70) and 0.07 mole (8 g.) of  $\text{C}_2\text{F}_5\text{H}$  (b. p. -48°, mol. wt. 115–119). Small amounts of  $\text{CF}_2\text{H}_2$  may also have been formed.

The lower layer, 27 g., gave no definite compounds although the relatively low molecular weights indicated that hydrogen compounds were present. For example, a fraction boiling at -18 to -11° had a mol. wt. of only 126. Some  $\text{C}_4\text{F}_{10}$ , 16.5 g., was recovered giving a total of 0.56 mole of  $\text{C}_4\text{F}_{10}$  recovered.

The results of the experiment at 840–850° were quite similar, the most notable difference being that the  $\text{CF}_3\text{H}$ : $\text{C}_2\text{F}_5\text{H}$  mole ratio was 4:1 as compared to the 2:1 ratio found at the lower temperature.

An attempt was made to identify other hydrogen compounds in the fractions boiling from -50 to -5°; the most probable of such compounds are  $\text{C}_2\text{F}_5\text{H}$ ,  $\text{CF}_2\text{H}_2$ ,  $\text{C}_2\text{F}_4\text{H}_2$  and  $\text{C}_3\text{F}_7\text{H}$ . The fractions boiling at -42 to -4°, 9.5 g., from 705° experiment were combined with fractions boiling -49° to -4°, 9.5 g., from 840° experiment; 14.5 g. of the mixture was brominated twice at 540–550°. Fractionation of the brominated products gave no definite compounds although there were indications of the formation of  $\text{C}_2\text{F}_5\text{Br}$  and possibly  $\text{C}_3\text{F}_7\text{Br}$ . Treatment of the bromine residues with potassium hydroxide yielded 3.5 g. of crude  $\text{C}_2\text{F}_4\text{Br}_2$ , mol. wt. 251–254; analysis by the sodium fusion method<sup>11</sup> gave Br, 60.0. Calcd. for  $\text{C}_2\text{F}_4\text{Br}_2$ : mol. wt., 260; Br, 61.5.

**Hydrogenolysis of Mixed Isomers of Cyclo- $\text{C}_6\text{F}_{12}$ .**—The starting material used in this experiment was a mixture of isomers of cyclo- $\text{C}_6\text{F}_{12}$  obtained from the mercury catalyzed fluorination of carbon; physical properties: b. p. 47–48.5°; mol. wt. 306–307. The mixture contained  $(\text{CF}_2)_6$  and at least one other isomer.<sup>12</sup> The hydrogenolysis was carried out in the carbon tube-lined reactor without the thermocouple well. Preliminary trials at 815–825° indicated that the cyclic material was of somewhat greater stability than saturated acyclic compounds so the experiment was carried out at 830–850°. The  $\text{C}_6\text{F}_{12}$ , 114 g. (0.38 mole) was mixed with hydrogen in a hydrogen: fluorocarbon mole ratio of 3:1 and passed through the reactor at a fluorocarbon flow rate of 0.10 mole per hour. The products were separated roughly into two portions: 65 g. boiling above 25° and 30 g. boiling below 25°. In addition 2 g. of carbon, corresponding to the decomposition of ca. 10 g. of fluorocarbon, was found.

Fractionation of the lower boiling product in column No. 1 gave 15.5 g. of  $\text{CF}_3\text{H}$  (b. p. -84 to -81°, mol. wt. 68.5–70). In addition, there was 3.5 g. (b. p. -54 to -36°, mol. wt. 72–77) which probably contained  $\text{CF}_2\text{H}_2$  since photochemical chlorination followed by fractionation gave 1.5 g. of material of mol. wt. 112–116, b. p. ca. -36°, assumed to be crude  $\text{CF}_2\text{Cl}_2$ .

The high boiling portion was fractionated in column No. 5 and proved to be mainly  $\text{C}_6\text{F}_{12}$ ; the recovered  $\text{C}_6\text{F}_{12}$ ,

(12) J. H. Simons and W. H. Pearlson, presented before the Division of Industrial and Engineering Chemistry of the American Chemical Society, New York, September, 1947.

48 g., was observed to have a higher melting point than the starting material.

The relatively high refractive indices and low molecular weights of other fractions indicated that hydrogen compounds were present. Fraction 5 was the largest such fraction; b. p. 42.0 to 45.0°; wt. 3 g.; mol. wt. 234-257;  $n_D^{20}$  1.288; H, 0.21. Hydrogen was determined by the method previously reported.<sup>13</sup>

The compound  $C_5F_8H$  has a calculated mol. wt. of 232 and hydrogen content of 0.43%. Other fractions decomposed slowly on storage. The evidence is inconclusive but indicates that cyclic hydrogen-containing fluorocarbons were produced. The virtual absence of hydrogen compounds of intermediate chain lengths (2 to 5 carbon atoms) is particularly evident in this experiment.

### Discussion

In all experiments with acyclic fluorocarbons the principal products isolated were  $CF_3H$  and  $C_2F_5H$ ; compounds having three or more carbon atoms per molecule were found only in small amounts. The initially formed products are apparently more reactive than the fluorocarbons themselves and react with hydrogen until  $C_2F_5H$  and especially  $CF_3H$  are formed. This process of carbon-carbon bond cleavage would be expected to yield considerable amounts of  $CF_2H_2$ , a product which was actually found only in small amounts. A rough calculation of the amount of  $CF_2H_2$  that could have been formed in the reaction of  $C_3F_8$  to account for the amounts of  $CF_3H$  and  $C_2F_5H$  isolated gives 19.8 g. of  $CF_2H_2$ . The carbon contained in 19.8 g. of  $CF_2H_2$  is 4.5 g., while the carbon formed during the reaction of  $C_3F_8$  with hydrogen weighed 5.5 g. While  $CF_2H_2$  may be quite unreactive under the reaction conditions,

(13) W. H. Pearson, T. J. Brice and J. H. Simons, *Ind. Eng. Chem., Anal. Ed.*, **18**, 330 (1946).

the data suggest that the  $CF_2$  group expected to appear in the final products as  $CF_2H_2$  is degraded by some process to carbon and (presumably) hydrogen fluoride.

The high temperature necessary for the reaction of the mixed isomers of  $C_6F_{12}$  with hydrogen illustrates the particular stability of cyclic fluorocarbons. Even under the rigorous conditions used the principal reaction observed was the cleavage of side chains, indicating that the parent ring compounds are still more stable. The fact that the recovered  $C_6F_{12}$  had a higher melting point than the starting material suggests that cyclic isomers having side chains reacted preferentially, leaving a mixture enriched in  $(CF_2)_6$ , the highest melting isomer.

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### Summary

Reactions of fluorocarbons with hydrogen at elevated temperatures have been studied. The principal products are those to be expected from the cleavage of carbon-carbon bonds in the presence of hydrogen,  $CF_3H$  and similar hydrofluorocarbons. The comparative stability of the cyclic fluorocarbons is demonstrated by their resistance to hydrogenolysis of the ring structure.

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## A Polarographic Study of $\beta,\gamma$ - and $\alpha,\beta$ -Angelica Lactones

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The marked differences noted<sup>2</sup> in the behavior of  $\beta,\gamma$ -angelica lactone and  $\alpha,\beta$ -angelica lactone upon catalytic hydrogenation suggested that a polarographic investigation of these unsaturated lactones should be of considerable interest. Such a study was undertaken, and solutions of both lactones were found to give well-defined reduction waves in the pH range 8.00-9.66. It soon became apparent, however, that the waves were obtained only for solutions of the lactones which gave positive qualitative tests for peroxides, and also that the magnitude of the diffusion current roughly paralleled the time of exposure to oxygen for any given solution. Hence the direction of the problem shifted to a quantitative study of the relationship between oxygen uptake and polarographic behavior of the lactones.

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(2) Jacobs and Scott, *J. Biol. Chem.*, **87**, 601 (1951).

### Experimental

**A. Preparation and Purification of Materials.**—Levulinic acid, technical grade, was purified by fractional distillation under reduced pressure. The fraction boiling at 101-102° at 3 mm., m. p. 30.3-31.2°, cor., was retained.

$\beta,\gamma$ -Angelica lactone was prepared and purified by the procedure of Thiele, Tischbein and Lossow<sup>3</sup>; b. p. 89-90° at 16 mm.,  $n_D^{20}$  1.4457.

$\alpha,\beta$ -Angelica lactone was prepared by isomerization of the  $\beta,\gamma$ -lactone in the presence of triethylamine according to the method of Thiele, *et al.*<sup>3</sup> Freed from unchanged  $\beta,\gamma$ -angelica lactone by the method of Wolff,<sup>4</sup> it boiled sharply at 83°;  $n_D^{20}$  1.4532.

2,3-Dihydroxyvalerolactone was prepared by oxidation of  $\alpha,\beta$ -angelica lactone with potassium permanganate according to the procedure of Thiele, *et al.*,<sup>3</sup> m. p. 100.1-101.3°, cor.

A series of buffer solutions was prepared according to Clark and Lubs as described by Kolthoff and Laitinen.<sup>5</sup> In all polarographic measurements for which data are

(3) Thiele, Tischbein and Lossow, *Ann.*, **319**, 180 (1901).

(4) Wolff, *ibid.*, **229**, 249 (1885).

(5) Kolthoff and Laitinen, "pH and Electro Titrations," John Wiley and Sons, Inc., New York, N. Y., 2nd ed., 1941, pp. 32-37.