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

Preparation and Some Properties of Certain Fluorovinyl Iodides and Some Fluorinated Butadienes[1]

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New fluorovinyl iodides, $CF_2{=}CHI$, $CF_2{=}CClI$, $CF_2{=}CBrI$, and $CF_2{=}CI_2$, were prepared and some of their reactions with various olefins studied. In all cases, a 1:1 linear adduct was formed, with the formation of small amounts of higher boiling fractions. A number of fluoro-1,3-butadienes were obtained from these adducts and their physical properties were tabulated.

This paper represents a continuation of our study on the preparation of certain fluorovinyl iodides[2] and some of their reactions under free radical and ionic conditions.

It was found that iodine monochloride added very readily to $CF_2{=}CH_2$, $CF_2{=}CHI$, $CF_2{=}CHBr$, and $CF_2{=}CHCl$ but more slowly to $CFCl{=}CFCl$. The additions to $CF_2{=}CH_2$ and $CF_2{=}CHI$ were very exothermic reactions, especially the latter, which was so vigorous that cooling was necessary during the course of the reaction.

The addition of iodine monochloride to these olefins is in agreement with the addition of alcohols under conditions favoring ionic reactions.[3-5] In our case, the negative chlorine becomes attached to the CF_2-group, which has a partial positive charge.

All of the olefins with the exception of $CFCl{=}CFCl$ gave yields of adducts ranging from 83% to 95%. 1,2-Dichloro-1,2-difluoroethylene gave a yield of 23% with a secondary product, $CFCl_2{-}CFCl_2$, being formed from the reaction: $CFCl_2CFClI + ICl \rightarrow CFCl_2CFCl_2 + I_2$ or from $CF_2ClCFClI$ and free chlorine (formed from the dissociation of ICl into iodine and chlorine). Very little, if any, secondary products were formed with the other olefins.

CF_2ClCHI_2 and $CFCl_2CFClI$ obtained from the iodine monochloride additions are very unstable to light and are extremely strong lachrymators and so unstable that no further reactions were attempted. On the other hand, $CF_2Cl{-}CH_2I$ has a pleasant odor and can be distilled at 92° with little or no decomposition.

The proof of structure of CF_2ClCH_2I, CF_2ClCHI_2, $CF_2Cl{-}CHBrI$, and $CF_2Cl{-}CHClI$, respectively, was established, chemically, by reaction with potassium hydroxide in mineral oil. In each case, a molecule of hydrogen chloride was removed with the formation of potassium chloride and $CF_2{=}CHI$, $CF_2{=}CI_2$, $CF_2{=}CBrI$, and $CF_2{=}CClI$, respectively. If the iodine monochloride had added the other way, to produce $CF_2I\text{-}CH_2Cl$ (in the case of $CF_2{=}CH_2$), a molecule of hydrogen iodide would have been removed. In addition, $CF_2Cl\text{-}CH_2I$ when treated with ethanolic potassium hydroxide yielded $CH_3CH_2OCF_2CH_2I$, the structure of which was proven by hydrolysis[6,7] of the ether with 96% sulfuric acid to the known ethyl iodoacetate. Similarly, $C_2H_5OCF_2CHClI$ upon hydrolysis yielded chloroiodoacetic acid.

Under free radical conditions the fluorovinyl iodides, $CF_2{=}CHI$, $CF_2{=}CClI$, $CF_2{=}CBrI$, and $CF_2{=}CI_2$ reacted with olefins in a manner such that the attacking free radical $CF_2{=}CX\cdot$ will add to a terminal CH_2-group, then a CFH-group and a CF_2-group, preferentially in that order as shown[2,8,9] previously in similar cases.

These additions ultimately resulted in the preparation of the following: 1,1-difluoro-2-chlorobutadiene; 1,1,2,4,4-pentafluoro-3-chlorobutadiene; 1,1-difluorobutadiene; and 1,1,4,4-tetrafluorobutadiene.

The reaction of $CF_2{=}CClI$ and $CF_2{=}CBrI$ apparently yielded Grignard reagents. These reacted with formaldehyde to yield $CF_2{=}CClCH_2OH$ and $CF_2{=}CBrCH_2OH$, respectively. However, we were unable to isolate any definite reaction products when the above Grignard reagents were treated separately with carbon dioxide and ethylene oxide.

The infrared spectra of all of the compounds prepared in this study were taken but are not reported in order to conserve space.

EXPERIMENTAL

The free radical addition reactions were carried out in Pyrex flasks which were sealed off at the neck and fitted

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[3] W. E. Hanford and G. W. Rigby, U. S. Patent **2,409,274**.

[4] W. T. Miller, Jr., E. W. Fager, and P. H. Griswold, *J. Am. Chem. Soc.*, **70**, 431 (1948).

[5] J. D. Park, D. K. Vail, K. R. Lea, and J. R. Lacher, *J. Am. Chem. Soc.*, **70**, 1550 (1948).

[6] J. A. Young and P. Tarrant, *J. Am. Chem. Soc.*, **71**, 2432 (1949).

[7] J. A. Young and P. Tarrant, *J. Am. Chem. Soc.*, **72**, 1860 (1950).

[8] R. N. Haszeldine and B. R. Steele, *J. Chem. Soc.*, 684 (1941).

[9] R. N. Haszeldine, *J. Chem. Soc.*, 473 (1952).

with stopcocks to permit the introduction and removal of the reactants and products. The ultraviolet light source was an Hanovia EH4 mercury arc tube.

1,1-Difluoro-2-iodoethylene (I). The dehydrochlorination of CF_2ClCH_2I (II) was carried out by a procedure similar to that previously reported[2] for the preparation of $CF_2{=}CFI$. It was found that better yields were obtained by running the reaction at about 200-mm. pressure.

The material was distilled over phosphorus pentoxide to yield 67 g. (65.4%) of a fraction boiling at 35.5° (622 mm.); n_D^{20} 2.171. Molecular weight determinations by the Regnault method: Calcd. for $CF_2{=}CHI$: 190. Found: 188.

Anal. Calcd. for C_2HF_2I: C, 12.64; H, 0.53; I, 66.8; F, 20. Found: C, 12.56; H, 0.58; I, 66.6; F, 19.8.

1,2-Dichloro-1,1-difluoro-2-iodoethane (III). The apparatus used in the addition of iodine monochloride to $CF_2{=}CHCl$ was a 5 × 35 cm. Pyrex tube with a sintered glass frit at the bottom for dispersion of the incoming gas and the top mounted by a reflux condenser connected in series to a bubble counter and a trap cooled to −78° for the collection of unreacted starting material.

In a typical run, 325 g. (2 moles) of iodine monochloride was placed in the apparatus described above, and 184 g. (1.9 moles) of $CF_2{=}CHCl$ passed through the glass frit from a steel cylinder at a rate such that some olefin came through the bubbler. The reaction, which is exothermic, required about 9 hr. The reaction product was washed with aqueous sodium bisulfite until colorless, then three more times with fresh water and finally dried over anhydrous sodium sulfate. Vacuum distillation in a Vigreux column yielded 442 g. (90%) of material boiling at 66–67° (100 mm.); n_D^{20} 1.4881; d_4^{20} 2.233.

Anal. Calcd. for $C_2HCl_2F_2I$: C, 9.2; F, 10.73. Found: C, 9.1; F, 10.58.

2-Chloro-1,1-difluoro-2-iodoethylene (IV). The dehydrochlorination of III was carried out in a 1-liter three-neck flask in a manner similar to that previously described[2] for $CF_2{=}CFI$. About 315 g. (0.82 mole) of III added dropwise to 90 g. (1.6 moles) of potassium hydroxide pellets suspended in 300 ml. of heavy mineral oil at 60° yielded 130 g. (78%) of III; b.p. 72–73° (628 mm.); n_D^{20} 1.4695; d_4^{20} 2.237.

Anal. Calcd. for C_2ClF_2I: C, 10.7; F, 16.9. Found: C, 11.0; F, 16.6.

1-Chloro-1,1-difluoro-2,2-diiodoethane (V). Into a 50-ml. three-neck flask, fitted with a dropping funnel, stirrer, and a reflux condenser, was placed 30 g. (0.16 mole) of I kept at 0°. Iodine monochloride was then added dropwise with stirring. The reaction was vigorously exothermic and was more easily controlled in another preparation by adding the olefin to ICl. The product was washed with aqueous $NaHSO_3$ and water, then dried with anhydrous sodium sulfate. Fifty-three g. of dried product was obtained. Distillation produced a 94% yield of V, b.p. 57.4–57.5° (8 mm.). The product is a very strong lachrymator and decomposes rapidly. A freshly redistilled sample was used for physical properties and analysis; b.p. 57.5° (8 mm.); n_D^{20} 1.5870; d_4^{20} 2.823.

Anal. Calcd. for $C_2HF_2ClI_2$: C, 6.82; F, 10.78. Found: C, 6.86; F, 10.99.

1,1-Dichloro-2,2-difluoroethylene (VI). A 50-ml. three-neck flask, equipped with a dropping funnel, a stirrer, and a reflux condenser, was charged with 20 g. powdered potassium hydroxide and 20 ml. $CFCl_2CF_2Cl$, the latter used as a medium for suspending the potassium hydroxide. Twenty-five g. of V was then added dropwise to the agitated mixture and the reaction initiated by bringing the solvent to a boil (43°). The addition of V was so adjusted to just keep the solvent ($CFCl_2CF_2Cl$) refluxing without external heat. A very hard salt cake was formed during the course of the reaction. Refluxing of the solvent was continued for 3 hr. after all the diiodide had been added. Distillation yielded 18.6 g. (83.5%) of VI, b.p. 133.5° (626 mm.); n_D^{20} 1.5869; d_4^{20} 2.961.

Anal. Calcd. for $C_2F_2I_2$: C, 7.6; F, 12.03. Found: C, 7.65; F, 11.95.

Reaction of $CF_2Cl{-}CH_2I$ and $CH_2{=}CH_2$. A. *Thermal reaction.* The iodide II (119 g., 0.53 mole) was put into a 500-ml. Parr hydrogenation bomb and charged to 450 lbs. per square inch with ethylene. The bomb was rocked for 20 min. and the pressure observed to insure no leakage. The reaction mixture was heated to 280° where a drop in pressure was noted. Heating at 280° was continued for an additional 3 hr. after which the bomb was allowed to cool off.

The unreacted ethylene was discharged through a series of traps cooled in Dry Ice. The liquid was transferred to an Erlenmeyer flask and stored in the deep-freeze. Carbon black and iodine were found on the walls of the bomb. The liquid product, which was a solid in the deep-freeze, was distilled on a Todd column. About 13.6 g. (10%) was obtained which had the extrapolated boiling point for the desired product, $CF_2ClCH_2CH_2CH_2I$ (VII). The fraction boiling at 44.3–44.7° (7 mm.) was taken as the desired product.

This fraction, which was iodine colored, was decolorized with aqueous sodium sulfite, washed with water, and dried over "Drierite." The compound is unstable to light; b.p. 41.5° (5 mm.); 67.5° (23 mm.); n_D^{20} 1.4780; d_4^{20} 1.867.

Anal. Calcd. for $C_4H_6ClF_2I$: C, 18.88; H, 2.38; I, 49.88. Found: C, 18.80; H, 2.60; I, 50.09.

Also isolated from the reaction was about 10 g. of ethylene iodide. This solid was purified by crystallization from warm petroleum ether (60–80°), sublimation under vacuum, and recrystallization from the same solvent. Long, needlelike crystals were obtained, m.p. 81°.

Anal. Calcd. for $C_2H_4I_2$: C, 8.52; H, 1.42. Found: C, 8.58; H, 1.36.

B. *Photochemical reaction.* About 23 g. (0.1 mole) of II and 3.5 g. (0.19 mole) of $CH_2{=}CH_2$ were placed in a three-liter Pyrex flask and irradiated with ultraviolet light. The reaction was allowed to continue for 14 days. Distillation was carried out in a micro-distillation apparatus. The first fraction was the starting iodide. The next fraction was 3.3 g. (13%) of VII coming over at 41.3° at about 6-mm. pressure, n_D^{21} 1.4790 (iodine colored), d_4^{20} 1.867.

Photochemical reaction of $CF_2{=}CHI$ and $CH_2{=}CH_2$. About 23 g. (0.1 mole) of I and 4.3 g. (0.15 mole) of $CH_2{=}CH_2$ were placed in a three-liter Pyrex flask and irradiated with an ultraviolet lamp for seven days. The resulting product was iodine colored. The reaction mixture was poured from the flask to a trap cooled in Dry Ice. Distillation through a Vigreux column afforded 10 g. (46%) of $CF_2{=}CH{-}CH_2{-}CH_2I$ (VIII) distilling at 58° (81 mm.). The sample was decolorized with a drop of mercury before use. The product gave a positive test for unsaturation with $KMnO_4$ in acetone. B.p. 45.0–45.3° (40 mm.); 69.0–69.2° (116 mm.); n_D^{20} 1.4752; d_4^{20} 1.863.

Anal. Calcd. for $C_4H_5F_2I$: C, 22.04; H, 2.31; I, 58.22. Found: C, 22.05; H, 2.28; I, 58.50.

1,1-Difluoro-1,3-butadiene (IX). A 50-ml. three-neck flask was equipped with a dropping funnel, a stirrer, and a reflux condenser whose outlet led to a trap cooled in Dry Ice. Fourteen ml. of light mineral oil and 8 g. of powdered potassium hydroxide were put into the flask and the stirred potassium hydroxide slurry was heated to 95°. Six grams (0.051 mole) of VIII was added dropwise to the KOH slurry. After about 2 hr., some liquid was found to be condensing in the cold trap. Heating and stirring was continued for 5 more hr., whereupon about two milliliters of liquid was obtained in the cold trap.

The molecular weight of the product was determined using a Regnault bulb. Molecular weight for IX: Calculated, 90.1. Found, 90.1. B.p. −1° at 630-mm. Hg. Tarrant[10] has previously prepared this compound by another route and reported a b.p. of +3.5° (760 mm.).

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(10) P. Tarrant, M. R. Lilyquist, and J. A. Attaway, *J. Am. Chem. Soc.*, **76**, 944 (1954).

TABLE I

PHYSICAL PROPERTIES OF COMPOUNDS PREPARED

			MR_D		AR_F	Mol. Wt.		
Compound	n_D^{20}	d_4^{20}	Calcd.	Found	Obsd.	Calcd.	Found	B.P., °C./Mm. Hg
$CF_2=CHI$	1.4376	2.171	23.77	22.95	0.69	190	188	33.5/622
$CF_2=CClI$	1.4695	2.237	28.49	27.95	0.76			73/628
$CF_2=CBrI$	1.5059	2.5837	31.53	30.91	0.79			95.5/622.5
$CF_2=CI_2$	1.5869	2.961	36.57	35.84	0.74			133.5/626
$CF_2Cl—CH_2I$	1.4655	2.166	29.10	28.92	1.01			92.3/624
$CFCl_2—CFClI$	$1.5017^{22°}$	$2.265^{22°}$	38.84	38.45	0.91			44.4/17
$CF_2Cl—CHClI$	1.4881	2.233	33.83	33.66	0.94			66/100
$CF_2Cl—CHBrI$	1.5229	2.5464	36.87	36.62	0.98			70.5/51; 139.5/628
$CF_2Cl—CHI_2$	1.5870	2.823	41.90	42.06	1.18			57.5/8
$CF_2ClCH_2CH_2CH_2I$	1.4870	1.867	38.34	38.59	1.22			41.5/5; 67.5/23
$CF_2=CH—(CH_2)_2I$	1.4752	1.863	33.00	32.96	1.08			45–45.3/20; 61.2/85; 69.0/116
$CF_2=CHCH_2CF_2I$	1.4193	1.909	33.01	33.62	1.25			86.9/631.5
$CF_2=CHCF_2CFClI$	1.4331	2.086	37.87	38.20	1.17			112/635
$CF_2=CClCH_2CH_2I$	1.4958	1.9724	36.84	37.37	0.80			142/631
$CF_2=CClCH_2CF_2I$	1.4435	2.024	37.88	37.81	0.87			120/627
$CF_2=CClCHFCF_2I$	1.4342	2.115	37.87	37.74	1.07			59/90
$CF_2=CHCH=CH_2$						90.1	90.1	
$CF_2=CHCH=CF_2$						127	126	−33.4/158; −5.5/509; −1.8/584
$CF_2=CClCF=CF_2$						175	178	30–32/630
$C_2H_5OCF_2CH_2I$	1.4520	1.794	35.12	35.48	1.28			62.1/59
$C_2H_5OCF_2CHClI$	1.4760	1.885	39.98	40.46	1.34			67/20
$CF_2=CClCH_2OH$	1.4028	1.4267	21.97	21.97	1.1			43/20

Photochemical preparation of $CF_2=CH—CH_2—CF_2I$ (X). In a manner similar to that described above, 33 g. (0.17 mole) of I and 20 g. (0.31 mole) of $CF_2=CH_2$ were irradiated with ultraviolet light in a five-liter flask for a period of 13 days. After this time, the contents of the flask were dissolved in ether and removed. Distillation was carried out in micro-equipment, after first removing the ether and unreacted I as one fraction. It is somewhat difficult to remove the last traces of ether from the higher boiling fractions. The fraction boiling at 42–44° (104 mm.) was taken as the desired product. Six grams (14% yield) of X was obtained. A test for unsaturation with $KMnO_4$ in acetone was positive. This product was decolorized with a drop of mercury before use. It is fairly stable to light. B.p. 86.9° (631.5 mm.); n_D^{20} 1.4193; d_4^{20} 1.909.

Anal. Calcd. for $C_4H_3F_4I$: C, 18.91; F, 29.92. Found: C, 18.87; F, 29.7.

1,1,4,4-Tetrafluoro-1,3-butadiene. A. *Dehydroiodination of* X. About 5.8 g. (0.023 mole) of $CF_2=CH—CH_2CF_2I$ was added dropwise to a stirred potassium hydroxide slurry heated to 95° and worked up in a manner similar to that described for compound IX. Two grams (83%) of XI was obtained; this showed a positive test for unsaturation with $KMnO_4$ in acetone. Molecular weight determination by the Regnault method for $CF_2=CHCH=CF_2$: Calculated, 126. Found, 127, b.p. (isoteniscope) −33.4° (158 mm.); −5.5° (509 mm.); −1.8° at 584-mm. Hg. The infrared spectra of the above with that of an authentic sample of $CF_2=CH—CH=CF_2$ were found to be superimposable.

B. *Wurtz-type reaction with* I. Eight to nine grams of sodium sand was prepared in 75 ml. of dibutyl ether in a 500-ml. Morton flask, the ether being distilled from sodium. The flask was fitted with a pressure equalizing dropping funnel, a mercury-sealed stirrer and a Dry Ice–cooled Friedrich condenser. Thirty grams of I dissolved in 25 ml. butyl ether was added dropwise while the reaction mixture was kept at 0°. Sodium iodide appeared to be forming, but it was difficult to tell due to the finely divided sodium present. The mixture was allowed to warm up to room temperature during the addition of the olefin.

After a total reaction time of about 7 hr., the coolant in the Friedrich condenser was allowed to warm to 5–10° and about two grams of liquid was collected in a cold trap connected to the condenser. Upon heating the reaction mixture further, the entire contents turned black indicating decomposition. Ten per cent yield of XI was obtained. The product gave a positive test for unsaturation with $KMnO_4$ in acetone. Molecular weight of $CF_2=CHCH=CF_2$. Calculated, 126; Found, 128. The infrared spectrum was the same as that obtained from the elimination of HI from X.

Photochemical reaction of $CF_2=CHI$ *and* $CF_2=CFCl$. About 38 g. (0.2 mole) of I and 33 g. (0.28 mole) of $CF_2=CFCl$ were placed in a three-liter evacuated Pyrex flask and irradiated with ultraviolet light for 13 days. After this period of time, the liquid and gaseous products were pumped out through a liquid nitrogen trap to give a total of 55 g. of material. This was then allowed to warm up to room temperature and the gaseous products removed. About 16 g. of high boiling liquid which remained was distilled. The fraction boiling at 74.5–75.0° (144 mm.) was taken as the desired product, $CF_2=CH—CF_2—CFClI$ (XII). In addition, a fraction (1.3 g.) distilling about 70° (8 mm.), n_D^{20} 1.4565 was obtained. This fraction was not identified. The yield of XII was 12.3%, based on I. All fractions were iodine colored and were decolorized with aqueous Na_2SO_3, washed with water, and dried over "Drierite." A test for unsaturation with $KMnO_4$ in acetone was positive, b.p. 112° (635 mm.); n_D^{20} 1.4331; d_4^{20} 2.086. This compound was considered too unstable to be sent for analysis.

Proof of the mode of addition of I to $CF_2=CFCl$ was established by attempting to dehalogenate the product with Zn. If addition had occurred to give $CF_2=CH—CFClCF_2I$, dehalogenation would have produced $CF_2=CH—CF=CF_2$, a butadiene previously prepared in this laboratory.[2] However, no pentafluorobutadiene was obtained in this dehalogenation.

Reaction of $CF_2=CHI$ *and* C_6H_6. Benzene and I were reacted photochemically in a five-liter flask for 13 days in an attempt to prepare $C_6H_5CH=CF_2$. During the course of the reaction a yellow-brown film was deposited on the inside of the flask. At the end of the reaction a considerable amount of free iodine was left in the flask. In the distillation, after removal of starting materials, about 0.5 ml. of a compound, distilling at 66° (61 mm.), and having an n_D^{20} of 1.4840, was obtained. This fraction showed a positive test for unsaturation with $KMnO_4$ in acetone. Prober[11] reports a b.p. of 65–66° (61–62 mm.); and an n_D^{20} of 1.4925 for $C_6H_5CH{=}CF_2$ prepared by another route.

Attempted coupling of C_6H_5MgBr and $CF_2Cl{-}CFClI$. Phenyl magnesium bromide (3*M* solution) was added dropwise to a stirred ethereal solution of $CF_2Cl{-}CFClI$ and a noticeable reaction took place with the deposition of a salt. However, no coupling product was obtained. Only phenyl iodide was isolated along with $CF_2{=}CFCl$. Similar results were obtained when the reaction was carried out at 0° and at −78°.

Photochemical reaction of $CF_2{=}CClI$ with $CH_2{=}CH_2$. About 45 g. (0.2 mole) of IV and 0.2 mole of ethylene were charged to a 5-liter Pyrex flask, sealed, and irradiated for 30 days. At the end of this period a good deal of iodine was present in the flask. The products of the reaction were obtained by pouring out the liquid and removing the vapors from the flask by suction. Distillation of the materials from the flask gave 11 g. of unreacted IV and 27 g. (71%) of the desired $CF_2{=}CCl{-}CH_2CH_2I$ (XIII), b.p. 142–143° (631 mm.); d_4^{20} 1.972; n_D^{20} 1.4958.

Anal. Calcd. for $C_4H_4F_2ClI$: C, 19.0%; F, 15.05%. Found: C, 18.95%; F, 15.1%.

1,1-Difluoro-2-chloro-1,3-butadiene. About 27 g. of XIII was treated with a suspension of mineral oil in a manner outlined in the preparation of IX. About 1 ml. of material was obtained. Attempts to obtain more product were unsuccessful. Enough material was available for an infrared spectrum which had the doublet associated with butadienes in the double bond region of the spectrum.[12]

Photochemical reaction of $CF_2{=}CClI$ with $CF_2{=}CHF$. About 45 g. of IV and about 0.2 mole of $CF_2{=}CHF$ were put into the 5-liter Pyrex bulb and irradiated with ultraviolet light for 18 days. After this period the products which were highly colored were removed from the flask. Distillation on a micro-distillation apparatus yielded 14 g. (69%) of $CF_2{=}CClCHFCF_2I$ (XIV) boiling at 58–59° (90 mm.). The iodine in the product was removed by shaking with a few drops of mercury and the physical properties were determined immediately after this treatment. n_D^{20} 1.4342; d_4^{20} 1.115.

Anal. Calcd. for C_4HClF_5I: C, 15.6; F, 31. Found: C, 15.46; F, 30.86.

1,1,3,4,4-Pentafluoro-2-chloro-butadiene. About 28 g. of XIV was added dropwise to a suspension of potassium hydroxide in mineral oil in a manner similar to that described for compound IX. Evacuation of the reaction system through a liquid nitrogen trap yielded 8 ml. of material. Pot to pot distillation of the reaction products in a vacuum system left about 0.5 ml. of product which was used for a molecular weight determination (Regnault method) and infrared spectrum. Mol. wt. Calcd. for $CF_2{=}CCl{-}CF{=}CF_2$: 178. Found: 175, b.p. 30–32° (628 mm.).

Anal. Calcd. for C_4F_5Cl: C, 26.9; F, 53.2. Found: C, 27.1; F, 53.

Infrared shows the doublet in double bond region of spectrum which is associated with butadiene.[12]

Photochemical reaction of $CF_2{=}CClI$ with $CF_2{=}CH_2$. A 5-liter Pyrex bulb was charged with 45 g. (0.2 mole) of IV and 0.2 mole of $CF_2{=}CH_2$ and irradiated with an ultraviolet light for 30 days. At the end of this period the products were highly colored with iodine. The contents of the flask were emptied and subjected to distillation in a micro-distillation assembly. About 14 g. of IV was recovered along with 19 g. of material boiling at 120° (627 mm.) which was the desired $CF_2{=}CCl{-}CH_2{-}CF_2I$ (XVI). Physical properties were determined after shaking the product with a few drops of mercury. n_D^{20} 1.4435; d_4^{20} 2.024. (AR$_F$ = 1.1).

Anal. Calcd. for $C_4H_2F_4ClI$: C, 16.66%; F, 26.35%. Found: C, 16.23%; F, 26.35%.

Preparation of Grignard reagent with $CF_2{=}CClI$. About 3 g. (0.13 mole) of magnesium turnings were washed with absolute ether and placed in a 300-ml. three-neck flask. The flask was provided with a reflux condenser, stirrer, and dropping funnel. After adding 100 ml. of absolute ether to the flask about 2 ml. of IV was added and the reaction started by warming the magnesium turnings in the flask with a pinpoint flame. A total of 22 g. of IV was added over a 2-hr. period at a rate such that reflux was maintained. The ethereal solution was quite dark at this point. The mixture was hydrolyzed with 100 ml. of 3*N* sulfuric acid and the gaseous products condensed in a trap cooled to −78°. Molecular weight determination (Regnault Method) gave a value of 95. Calcd. for $CF_2{=}CHCl$ is 98.5.

Reaction of $CF_2{=}CClMgI$ with formaldehyde. Preparation of the Grignard reagent was carried out in a 500-ml. Morton flask provided with a stirrer, 0° reflux condenser, and a dropping funnel with a pressure equalizing arm. About 5 g. of magnesium turnings were washed with absolute ether, placed in the Morton flask, and covered with 100 ml. of ether. The Grignard reaction was initiated in the usual way and a total of 42 g. (0.19 mole) of IV was added dropwise over a 3-hr. period, while the ethereal solution of the Grignard reagent was stirred vigorously, and cooled with an ice bath. Seven grams of paraformaldehyde was depolymerized by heating and the gaseous formaldehyde was led into the reaction mixture through a section of 10-mm. glass tubing set just above the surface of the ether. During the addition of the formaldehyde, enough heat is generated to cause refluxing of the ether. After the formaldehyde was added, the mixture was allowed to come to room temperature and stirred for an additional 3 hr. At the end of this period the reaction mixture was poured on cracked ice and acidified with 100 ml. of 20% sulfuric acid. The ether layer was separated and the aqueous layer was extracted with three 100-ml. portions of ether. The ether fractions were combined, and dried over anhydrous potassium carbonate over night. The ether was stripped off with a vacuum pump leaving a tarry liquid which was subjected to vacuum distillation through a Vigreux column. About 14 g. (54%) of a colorless liquid, b.p. 42–43° (20 mm.) was obtained. This liquid which was the desired $CF_2{=}CClCH_2OH$ reacted with sodium metal, gave a positive test for unsaturation with aqueous potassium permanganate, and an acid reaction to litmus. n_D^{20} 1.4028; d_4^{20} 1.427.

Anal. Calcd. for $CF_2{=}CClCH_2OH$: C, 28; F, 29.6. Found: C, 28.1; F, 29.2.

Attempted coupling of $CF_2Cl{-}CH_2I$. A 1-liter three-neck flask was provided with a stirrer, dropping funnel, and a reflux condenser. This assembly was charged with 160 ml. of acetic anhydride, 160 ml. of methylene chloride, and 65 g. (1 mole) of zinc dust. About 226 g. (1 mole) of II was added slowly. No reaction occurred at room temperature; however, heating with a microburner caused some dehalogenation as shown by the presence of a low boiling liquid in the traps which was $CF_2{=}CH_2$ and would result from the dehalogenation of the starting material. None of the desired $CF_2ClCH_2CH_2CF_2Cl$ was obtained.

Attempted reaction of $CF_2ClCFClI$ with $CF_2{=}CHCl$. A 500 ml.-Parr bomb was sealed, cooled in an isopropyl alcohol-Dry Ice bath and evacuated. The bomb was checked for leaks by sealing the bomb and letting it stand for 10 min. and checking for any loss in vacuum by means of a mercury manometer connected to the bomb. The bomb was then charged with 150 g. (0.55 mole) of $CF_2ClCFClI$ and 55 g. (0.55 mole) of $CF_2{=}CHCl$. After warming to room temperature, the bomb was heated to 200° while being rocked. About 500 p.s.i. showed on the gauge during the 8-hr. rocking period. At the end of the period the bomb was allowed to cool and the unreacted olefin was collected in a series of traps cooled to −78°. Almost all of the unreacted olefin was collected. Apparently, no reaction took place.

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[11] M. Prober, *J. Am. Chem. Soc.*, **75**, 968 (1953).

[12] L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, 1st ed., Wiley & Sons, Inc., N. Y., 1954, p. 35.

Attempted Grignard reactions with $CF_2{=}CClMgI$. The Grignard reagent was synthesized with IV on a 0.2*M* basis as described previously. The reagent was then allowed to react with 0.2*M* quantities each of ethylene oxide, carbon dioxide, perfluorobutyronitrile, and lithium perfluorobutyrate, respectively. However, no reaction product was isolated in each case.

Attempted reaction of $CF_2ClCFClI$ with SO_2. A 500-ml. stainless steel Parr bomb was sealed and checked for leaks by evacuating, sealing, and checking for loss of vacuum with a mercury manometer. About 160 g. (0.55 mole) of $CF_2ClCFClI$ containing 0.1 g. of benzoyl peroxide was charged to the bomb. After cooling the bomb to −78° about 30 g. of sulfur dioxide was allowed to pass in. The bomb was then heated to 100° and left at this temperature over night. Distillation of the products from the bomb yielded only the starting $CF_2ClCFClI$.

Attempted Grignard formation with $CF_2ClCFClI$. About 23 g. (0.2 mole) of $CF_2Cl{-}CFCl$ was added to 5 g. of magnesium covered with 100 ml. of tetrahydrofuran dried over sodium. The reaction was initiated in the usual way and the rest of the iodide was added dropwise over a 1-hr. period. The magnesium was consumed at the end of this period and a low boiling liquid had condensed in the trap attached to the reflux condenser. A molecular weight determination on this gave a value of 114, theory for $CF_2{=}CFCl$ is 116. Hydrolysis of the reaction mixture with 20% sulfuric acid did not yield other products. Apparently the only reaction which had occurred was that of dehalogenation.

Attempted Grignard reaction with $CF_2{=}CHI$. In an attempt to prepare the Grignard reagent, $CF_2{=}CHMgI$, I was treated with an equivalent amount of magnesium in sodium dried diethyl ether. The reaction was run under conditions identical to those in which perfluorovinyl iodide, $CF_2{=}CFI$, was shown to react quite rapidly.[2] After a period of 16 hr., it was visibly evident that none or very little of the magnesium had reacted.

1,1-Difluoro-1-chloro-2-bromo-2-iodoethane (XVII). The preparation and purification of XVII was carried out with $CF_2{=}CHBr$ and ICl in a manner similar to that previously described[2] for the preparation of $CF_2Cl{-}CFClI$. Yield 83%, b.p. 70.5° (51 mm.); 139.5–140° (628 mm.); n_D^{20} 1.5229; d_4^{20} 2.5464.

Anal. Calcd. for $C_2HBrClF_2I$: C, 7.85; F, 12.44. Found: C, 7.9; F, 12.3.

1,1-Difluoro-2-bromo-2-iodoethylene (XVIII). About 30 g. of powdered potassium hydroxide suspended in 90 ml. of $CF_2Cl{-}CFCl_2$ was placed in a 100-ml. three-neck flask equipped with stirrer, dropping funnel, and reflux condenser. About 46 g. (0.15 mole) of XVII was added dropwise to the above suspension in the course of an hour. Heat was maintained as the reflux boiling point of $CF_2Cl{-}CFCl_2$. Stirring was continued for an additional 2 hr., after which the reaction products were decanted and stored over "Drierite." Distillation of the products yielded 31.5 g. (78%) of XVIII with the following properties. B.p. 95.5° (622.5 mm.); n_D^{20} 1.5059; d_4^{20} 2.5837.

Anal. Calcd. for C_2BrF_2I: C, 8.93; F, 14.13. Found: C, 8.81; F, 14.05.

Preparation of $CF_2{=}CBrMgI$. About 4 g. (0.165 mole) of magnesium turnings and 43 g. of XVIII were reacted according to the procedure outlined for the preparation of $CF_2{=}CClMgI$. Hydrolysis of the Grignard reagent with 4*N* sulfuric acid yielded a gas of molecular weight (Regnault method) of 145. Calcd. for $CF_2{=}CHBr$ is 143.

Reaction of $CF_2{=}CBrMgI$ with formaldehyde. The Grignard reagent was treated with formaldehyde in a manner similar to that described for the preparation of $CF_2{=}CCl{-}CH_2OH$. A yield of 20 g. (56%) of $CF_2{=}CBrCH_2OH$ was obtained. B.p. 35.5–36° (5 mm.); n_D^{20} 1.4469; d_4^{20} 1.8966.

Anal. Calcd. for $C_3H_3BrF_2O$: C, 20.83; H, 1.73; F, 21.94. Found: C, 20.78; H, 1.88; F, 21.79.

Attempted reactions with $CF_2{=}CBrMgI$. The Grignard reagent was allowed to react with solid carbon dioxide and ethylene oxide, respectively. No reaction product was isolated in either case.

1,1-Difluoro-2-iodoethyl ethyl ether (XIX). Thirty grams of potassium hydroxide dissolved in 100 ml. of absolute ethanol was placed in a 300-ml. three-neck flask fitted with a reflux condenser, stirrer, and dropping funnel. Under reflux, 68 g. (0.3 mole) of II was added during a period of 30 min. The heat generated from the reaction was sufficient to maintain refluxing of the alcohol. Stirring was continued for an additional 2 hr. The product being unstable produced some free iodine in solution.

Water was added to the ethanol solution and two layers formed were separated, washed, and dried over sodium sulfate.

Distillation on the platinum-spiral Todd column showed that everything except a small amount of very high boiler distilled at 62.1° (59 mm.). 54 g. (76.5%) of XIX was obtained, b.p. 62.1° (59 mm.); n_D^{20} 1.4520; d_4^{20} 1.794.

This ether is a strong lachrymator and very unstable to light.

Further proof of its structure was established by hydrolyzing this ether to the known ester, $CH_2ICOOCH_2CH_3$, b.p. 73–74° (16 mm.); n_D^{19} 1.5043. Beilstein reports a b.p. 73° (16 mm.) and $n_D^{12.5}$ 1.5079.

1,1-Difluoro-2-chloro-2-iodoethyl ethyl ether (XX). About 52 g. of III was added dropwise to 100 ml. of 12% ethanolic potassium hydroxide in a manner similar to that described for the preparation of XIX. Distillation of this compound at 20 mm. gave 16 g. (30%) of product boiling at 66–67°. The compound was quite lachrymatory and liberated iodine on standing. The iodine color was removed by shaking the compound with a few drops of mercury and physical properties were immediately determined. n_D^{20} 1.4760; d_4^{20} 1.885.

The hydrolysis of $C_2H_5OCF_2CHClI$ was carried out in the following manner. About 16 g. of XX was charged to a 150-ml. three-neck flask provided with a stirrer, reflux condenser, and a dropping funnel. Stirring was started and 50 ml. of 90% sulfuric acid was added dropwise. After the addition of the sulfuric acid was completed the mixture was heated at 95° on a water bath and stirred for an additional hour. A white solid which was silicon dioxide was found in the water trap attached to the reflux condenser indicating that the CF_2 group was being hydrolyzed.

The reaction mixture was then poured into 200 ml. of water. Extraction of the aqueous mixture with ether was followed by extraction of the ether with 5% sodium hydroxide solution. Neutralization of the aqueous solution was followed by ether extraction. Evaporation of the ether solution left about 3 g. of solid. Recrystallization from cyclohexane gave a white solid melting at 89.5–90° (Willstatter[13] reports an m.p. of 90° for $CHClICO_2H$).

The ether solution which should contain the ester, $CHClI{-}CO_2C_2H_5$ was treated with anhydrous ammonia. Evaporation of the ether left a solid which was recrystallized from cyclohexane. M.p. 140° (literature[13] reports 140° for $CHClI{-}CONH_2$).

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BOULDER, COLO.

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(13) R. Willstatter and H. F. Hattenroth, *Ber.*, **37**, 1775 (1904).