thiosulfate, saturated calcium chloride, water and dried over anhydrous sodium sulfate. The solvent was stripped and the residual oil fractionated through a Wheeler column to yield 23 g. (32%) of product, b.p. 143°, n^{30}_D 1.4362.

Anal. Calcd. for $C_5H_8F_3I$: C, 23.83; H, 3.20. Found: C, 23.78; H, 3.32.

5-Methyl-6,6,6-trifluoronorleucine.—To a suspension of 0.70 g. (0.29 mole) of sodium hydride in 12 cc. of anhydrous N,N-dimethylformamide was added 5.5 g. (0.27 mole) of diethyl formamidomalonate. After 10 minutes the solution was filtered and the filtrate added to 7.3 g. (0.29 mole) of 2-methyl-4,4,4-trifluorobutyl iodide dissolved in 2 cc. of dimethylformamide. The mixture was heated at 130° for 0.5 hr. and at 160° for two hours. The solvent was removed *in vacuo* and the residue triturated with ether. The ether extract was stripped and the residue refluxed with 75 cc. of 2:1 hydrochloric acid for 5 hours. The solution was evaporated to dryness *in vacuo* and the solids taken up in ethanol. The ethanolic solution was made basic with pyridine and cooled. The solid which deposited was filtered and recrystallized from water to yield 200 mg. of amino acid, m.p. 254–256° dec.

Anal. Calcd. for $C_7H_{12}F_3NO_2$: C, 42.20; H, 6.07. Found: C, 42.28; H, 6.20.

TALLAHASSEE, FLORIDA

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

Free Radical Additions Involving Fluorine Compounds. V. Reactions of 1,2-Dibromo-2-chloro- and 1,2-Dichloro-2-iodo-1,1,2-trifluoroethane with Fluoroölefins[1]

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A study has been made of the reaction of 1,2-dibromo-2-chloro- and 1,2-dichloro-2-iodo-1,1,2-trifluoroethane with various fluoroethenes and fluoropropenes. The iodine compound gives excellent yields of addition products even with olefins which fail to react with the dibromide. The high yields of adducts from these perhaloethanes and the ease with which these addition compounds can be dehydrohalogenated and dehalogenated afford a good synthetic method of preparation of various fluoroölefins and 1,1,2-fluorobutadienes.

Earlier reports from this Laboratory have described the reactions of dibromodifluoromethane,[2] bromochlorodifluoromethane[3] and 1,2-dibromo-2-chloro-1,1,2-trifluoroethane[4] with various olefins. The resulting simple addition products were converted into fluoroölefins by dehydrobromination or into fluorobutadienes by suitable reactions. For example, various 1,1-difluorobutadienes were obtained by heating the adducts of dibromodifluoromethane and propenes with tri-*n*-butylamine and a number of 1,1,2-trifluoro-1,3-alkadienes were obtained from adducts of the perhaloethane.

The preparation of 1,1,2-trifluoro-1,3-butadiene has been carried out earlier in these laboratories[5] by the reactions

$$CF_2Br_2 + CHF{=}CHCH_3 \xrightarrow[\text{peroxide}]{\text{benzoyl}}$$

$$CF_2BrCHFCHBrCH_3 \xrightarrow{R_3N} CF_2{=}CFCH{=}CH_2$$

but, because of the present difficulty in obtaining 1-fluoropropene, this method is not practical for preparing large samples of the diene. The synthesis of 1,1,2-trifluoro-1,3-butadiene recently has been reported by Park, Seffl and Lacher[6] in a six-step process involving the addition of perfluorovinyl iodide to ethene. We wish to report that this butadiene also has been prepared from 1,4-dibromo-2-chloro-1,1,2-trifluorobutane[4] by removal of hydrogen bromide to give $CF_2BrCFClCH{=}CH_2$ which, when treated with zinc, gives $CF_2{=}CFCH{=}CH_2$.

Although 1,2-dibromo-2-chloro-1,1,2-trifluoroethane (I) was found to react readily with most hydrocarbon olefins to give good yields of the addition products, $CF_2BrCFClCH_2CHBrR$, the yields of addition products from olefins containing several fluorine atoms are reduced greatly. For instance, fluoroethene gave a 74% yield of $CF_2BrCFClCH_2CHFBr$, but trifluoroethene gave only 16% of the simple adduct, and 1-chloro-1-fluoroethene and 1,1-difluoropropene failed to form any adduct. It should be noted that increasing amounts of fluorine around the double bond of the olefin led to the formation of larger quantities of two-to-one addition products.

Previous work[4] on the addition of I to hydrocarbon olefins has demonstrated that the $CF_2BrCFCl$ group remains intact during addition reactions so that the proof of structures of the one-to-one adducts from fluoroölefins involves only the problem of the point of attachment of that group to the double bond. The simple products from 1,1-difluoro- and trifluoroethene could have only the structures of $CF_2BrCFClCH_2CF_2Br$ and $CF_2BrCFClCHFCF_2Br$, respectively, since hydrogen bromide was eliminated readily to give olefins. The structure of the adduct from fluoroethene and I was assigned on the basis of the similarity of the reaction to that with dibromodifluoromethane and fluoroethene, which gave an adduct which has been shown to have the formula CF_2BrCH_2CHFBr.[5] The assignment of structures to the higher adducts is consistent with the mechanism which postulates that the alkyl radical attacks the carbon atom of the double bond containing the greater number of hydrogen atoms.

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[1] This research was supported by Contract DA44-109-qm-1469 between the Office of the Quartermaster General and the University of Florida with Dr. J. C. Montermoso as Project Officer.

[2] P. Tarrant and A. M. Lovelace, THIS JOURNAL, **76**, 3466 (1954).

[3] P. Tarrant and A. M. Lovelace, *ibid.*, **77**, 768 (1955).

[4] P. Tarrant and E. G. Gillman, *ibid.*, **76**, 5423 (1954).

[5] P. Tarrant, A. M. Lovelace and M. R. Lilyquist, *ibid.*, **77**, 2783 (1955).

[6] J. D. Park, R. J. Seffl and J. R. Lacher, Abstracts of Papers, 126th National Meeting of the American Chemical Society, New York, N. Y., September, 1954.

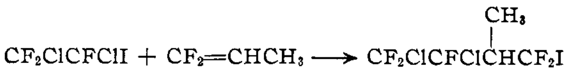
The adducts of I and fluoroölefins can be dehydrohalogenated readily by refluxing with aqueous alkali, although the conversion of $CF_2BrCFClCH_2CH_2Br$ to $CF_2BrClFCCH{=}CH_2$ required alcoholic potassium hydroxide. Yields of olefins were good in most cases, probably because the formation of ethers as by-products was minimized. These olefins were transformed into 1,3-butadienes by treatment with zinc. The properties of these compounds are given in Table II.

In order to develop a synthetic method for the preparation of olefins and dienes which could not be made from I, a study was made of the reaction of 1,2-dichloro-2-iodo-1,1,2-trifluoroethane[7] (II) with various fluoroölefins. The simple adduct of II and trifluoroethene was obtained in a 79% yield and 1-chloro-1-fluoroethene gave 45% of adduct. In the fluoropropene series, 3,3,3-trifluoropropene formed an addition product in 95% yield while 1,1-difluoropropene, which failed to react with $CF_2BrCFClBr$, gave 89% of the simple adduct, 2-trifluoromethylpropene, which did not react with dibromodifluoromethane at 100° in the presence of benzoyl peroxide,[5] reacted with II to give 87% of adduct. It is thus evident that the use of II in reactions leads to amounts of adducts close to the theoretical value even with relatively unreactive olefins. It is to be expected that correspondingly high yields of simple products would be obtained from the hydrocarbon olefins and II.

Neither perfluoropropene nor 1,1,3,3,3-pentafluoropropene reacted with $CF_2ClCFClI$ to give any simple addition product.

As would be expected, peroxide-catalyzed reactions of II involve the scission of the carbon–iodine bond to give the radical $CF_2ClCFCl\cdot$ which then adds to fluoroölefins in the same direction as does $CF_2BrCFCl\cdot$. For example, trifluoroethene and II gave $CF_2ClCFClCHFCF_2I$ since the known[8] $CF_2ClCFClCF{=}CF_2$ and $CF_2{=}CFCF{=}CF_2$ were obtained by dehydrohalogenation and subsequent dehalogenation. The adduct from 1-chloro-1-fluoroethene also lost hydrogen iodide when treated with base thus demonstrating that its structure is $CF_2ClCFClCH_2CFClI$. The addition product from 2-trifluoromethylpropene must have the structure $CF_2ClCFClCH_2C(CF_3)ICH_3$ rather than $CF_2ClCFClC(CF_3)(CH_3)CH_2I$ since the latter could not be converted to a simple olefin, whereas the adduct readily lost hydrogen iodide.

The addition of II to 1,1-difluoropropene is interesting because the alkyl radical attacks the carbon atom containing hydrogen rather than the difluoromethylene group.



$$CF_2ClCFClI + CF_2{=}CHCH_3 \longrightarrow CF_2ClCFCl\overset{\overset{\displaystyle CH_3}{|}}{C}HCF_2I$$

This resistance of the $CF_2{=}$ group toward radical attack has been reported earlier by Haszeldine,[9] who obtained $CF_3CH(CH_3)CF_2I$ from the reaction of trifluoromethyl iodide and 1,1-difluoropropene. The infrared spectrum of the olefin obtained by removal of hydrogen iodide from the adduct of II and 1,1-difluoropropene had an absorption maximum at 5.73 μ, which is the region characteristic of compounds containing the $CF_2{=}$ structure, showing the adduct to have the structure $CF_2ClCFClCH(CH_3)CF_2I$ rather than $CF_2ClCFClCF_2CHICH_3$ since the latter compound, if it lost hydrogen iodide, would give an olefin containing the $—CH{=}CH_2$ group, which has its characteristic absorption above 6.0 μ.

It has been demonstrated that free radical additions of perhalomethanes to 3,3,3-trifluoropropene give compounds of the type $CX_3CH_2CHXCF_3$.[10] The presence of the $CF_3CH{=}CH—$ group in the olefin obtained by dehydrohalogenation of the adduct of II and $CF_3CH{=}CH_2$ is indicated by infrared absorption at 5.92 μ thus showing that the attacking $CF_2ClCFCl\cdot$ radical added to the terminal carbon atom of the double bond.

The products from II and the fluoroölefins were converted readily to olefins containing the $CF_2ClCFCl$ group adjacent to the double bond. These olefins react with zinc to give the conjugated dienes containing the perfluorovinyl group.

A number of interesting fluorobutadienes were obtained conveniently and in good yield starting with $CF_2BrCFClBr$ or $CF_2ClCFClI$. For example, 1,1,2-trifluorobutadiene has been obtained in an over-all yield of 27% from I and ethene in a three-step synthesis; perfluorobutadiene has been obtained from II and trifluoroethene in 40% yield; 1,1,2,4,4-pentafluorobutadiene from II and 1,1-difluoroethene in 32% yield; and 2-methylperfluorobutadiene was synthesized from II and 1,1-difluoropropene in 37% yield. The properties of the olefins and dienes obtained in this research are shown in Table II.

Experimental

Additions of 2-Chloro-1,2-dibromo- and 1,2-Dichloro-2-iodo-1,1,2-trifluoroethane to Olefins.—All addition reactions were carried out using either a 1.4-l. or a 300-ml. stainless steel rocking autoclave. In the cases where the olefin could not be readily condensed by a Dry Ice–acetone mixture, it was introduced indirectly from a storage cylinder through a valve and gage assembly attached to the autoclave. Otherwise the clave was cooled in Dry Ice and acetone and the liquefied reactants were added before sealing the reaction vessel. In all reactions, unless otherwise stated, benzoyl peroxide was used as the catalyst and the reaction vessel was maintained at 100° for a period of four hours. The products were separated by distillation through a 42-cm. column packed with glass helices. The properties of these compounds are given in Table I.

In a typical peroxide-catalyzed addition reaction 2-chloro-1,2-dibromo-1,1,2-trifluoroethane (1073 g., 3.9 moles) and 1,1-difluoroethane (122 g., 1.9 moles), treated as described above, gave 282 g. of the simple adduct V and 123 g. of the two-to-one addition product VI.

Reaction of 1,2-Dibromo-2-chloro-1,1,2-trifluoroethane with 1,1-Difluoropropene-1.—In the manner described, I (370 g., 1.36 mole) was treated with 1,1-difluoropropene-1 (26 g., 0.33 mole) giving only the unreacted materials and 25 g. of tarry substance.

Reaction of 1,2-Dichloro-2-iodo-1,1,2-trifluoroethane and Perfluoropropene.—Compound II (407 g., 1.46 moles) and perfluoropropene (40 g., 0.29 mole) reacted, giving only recovered starting material and 15 g. of a tarry residue.

Reaction of 1,2-Dichloro-2-iodo-1,1,2-trifluoroethane and 1,1,3,3,3-Pentafluoropropene.—When II (350 g., 1.25 moles) and 1,1,3,3,3-pentafluoropropene (35 g., 0.26 mole)

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[8] W. T. Miller, National Nuclear Energy Series, Div. VII. 1, Prepn. Properties and Technol. of Fluorine and Organic Fluorine Compounds, 1951, p. 567.

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[10] A. L. Henne and M. Nager, THIS JOURNAL, **73**, 5527 (1951).

TABLE I

THE PROPERTIES OF THE ADDITION PRODUCTS OF FLUOROÖLEFINS AND HALOETHANES

Olefin	Addition product	Yield, %	B.p., °C.	Mm.	n^t_D	d^t_4	t, °C.	MR_D[a] Calcd.	Found	Silver equiv. Calcd.	Found
$CH_2{=}CHF$	$CF_2BrCFClCH_2CHFBr$ (III)	74	72	32	1.4405	2.075	25	41.08	41.00	107.4	106.5
	$CF_2BrCFClCH_2CHFCH_2CHFBr$ (IV)	6.4	104.5	15	1.4428	1.946	27	50.30	50.13	122.8	122.7
$CH_2{=}CF_2$	$CF_2BrCFClCH_2CF_2Br$ (V)	44	70.1	50	1.4230	2.063	27	41.08	41.03	113.4	111.9
	$CF_2BrCFClCH_2CF_2CH_2CF_2Br$ (VI)	23.4	90–91	20	1.4112	2.014	27	49.61	50.30	134.7	133.6
$CHF{=}CF_2$	$CF_2BrCFClCHFCF_2Br$ (VII)	16.2	61.5	40	1.4330	2.013	23	41.07	46.27	116.1	116.4
	$CF_2BrCFClCHFCF_2CHF$-CF_2Br (VIII)	20	79.5	15	1.3943	2.077	25	50.31	50.75	146.8	147.0
$CH_2{=}CFCl$	$CF_2ClCFClCH_2CFClI$ (IX)	45	70	10	1.4741	2.075	22	48.07	48.68	89.8	90.0
$CHF{=}CF_2$	$CF_2ClCFClCHFCF_2I$ (X)	79	56	23	1.4224	2.110	28	43.21	43.49	120.3	120.0
$CH_2{=}CHCF_3$	$CF_2ClCFClCH_2CHI(CF_3)$ (XI)	95	61	18	1.4275	2.013	22	48.72	47.91	125.0	125.9
$CF_2{=}CHCH_3$	$CF_2ClCFClC(CH_3)HCF_2I$ (XII)	89	75.5	20	1.4567	1.994	25	47.82	48.72	119.0	119.2
$CH_2{=}\underset{CF_3}{C}CH_3$	$CF_2ClCFClCH_2C(CF_3)ICH_3$ (XIII)	87	65.5	12	1.4418	1.947	22	52.45	52.84	129.6	129.2

[a] Value 1.1000 was used as atomic refraction for fluorine.

TABLE II

THE PROPERTIES OF OLEFINS AND DIENES OBTAINED FROM THE ADDITION PRODUCTS OF OLEFINS AND PERHALOETHANES

Compound	B.p., °C.	n^t_D	d^t_4	t, °C.	MR^a_D Calcd.	Found	Analyses Calcd.	Found	Infrared absorption,[i] μ
$CF_2BrCFClCH{=}CH_2$ (XIV)	99.5	1.4092	1.678	25	32.84	32.93	111.7	113.4[b]	6.07
$CF_2{=}CF{-}CH{=}CH_2$[h] (XV)	7.8–8.0						108.1	109.5[c]	5.53, 5.66
$CF_2BrCFClCH{=}CHF$ (XVI)	97–97.3	1.3961	1.781	25	32.44	32.58	120.7	121.3[b]	5.70, 5.93
$CF_2{=}CF{-}CH{=}CHF$ (XVII)	16.5	1.3427	1.342	0	19.74	19.84	126.1	122.8[c]	5.62, 5.80, 6.02
$CF_2BrCFClCH{=}CF_2$ (XVIII)	91.0	1.3837	1.838	24	32.84	32.97	129.7	130.2[b]	5.72
$CF_2{=}CF{-}CH{=}CF_2$ (XIX)	15.5						144.1	145.2[c]	5.58, 5.78
$CF_2ClCFClCF{=}CF_2$[g] (XX)	65.5–67	1.3440	1.615	22	29.9	30.5			5.60
$CF_2{=}CF{-}CF{=}CF_2$[g] (XXI)	7.1–7.3								5.55, 5.64
$CF_2ClCFClC(CH_3){=}CF_2$ (XXII)	100.5	1.3746	1.515	22	34.56	34.64	31.3	31.4[d]	5.73
$CF_2{=}CF{-}C(CH_3){=}CF_2$ (XXIII)	37.0	1.3250	1.289	20	24.36	24.68	37.92 1.91	38.12[e] 1.90[f]	5.59, 5.74
$CF_2ClCFClCH{=}C(CH_3)CF_3$ (XXIV)	109.5	1.3675	1.485	20	39.18	39.51	27.20	26.9[d]	5.92
$CF_2{=}CF{-}CH{=}C(CH_3)CF_3$ (XXV)	71.5	1.3531	1.350	22	28.98	30.50	37.91 2.12	37.72[e] 2.08[f]	5.71, 5.80
$CF_2ClCFClCH{=}CHCF_3$ (XXVI)	87.5	1.3472	1.519	23	34.56	34.78	28.75	29.0[d]	5.92
$CF_2{=}CF{-}CH{=}CH{-}CF_3$ (XXVII)	50.5	1.3322	1.389	22	24.36	26.01	34.11 1.15	33.90[e] 1.26[f]	5.68, 5.98
$CF_2ClCFClCH{=}CFCl$ (XXVIII)	102.5	1.3993	1.586	24	34.81	35.28	45.96	45.7[d]	5.95
$CF_2{=}CF{-}CH{=}CFCl$ (XXIX)	53.0	1.3804	1.431	24	24.6	25.9	22.1	22.3[d]	5.65, 6.02

[a] Atomic refraction fluorine 1.100. [b] Silver equivalent. [c] Molecular weight. [d] Chlorine, %. [e] Carbon, %. [f] Hydrogen, %. [g] Previously reported by W. T. Miller, Jr. (see ref. 8). [h] Previously reported (see ref. 11). [i] Determined on Perkin-Elmer model 21. Absorption peaks in carbon–carbon double bond region.

were treated in the usual manner, only the reactants were recovered. Similar results were obtained when the reaction was repeated at 150° using di-*t*-butyl peroxide as the catalyst.

The Preparation of the Olefins.—A typical dehydrohalogenation of the adducts of I and II with olefins follows.

A saturated solution of potassium hydroxide (3 moles) in propanol-1 (1000 ml.) was added dropwise to heated 2-chloro-1,4-dibromo-1,1,2-trifluorobutane (1 mole), obtained from I and ethene, in a 2-l. flask equipped with a stirrer, addition funnel and variable rate take-off distilling head. A mixture of the olefin and propanol was distilled as the reaction proceeded. This material was washed well with water and dried over calcium chloride. Fractionation of the dried product through a 42-cm. column packed with glass helices gave 150 g. (68%) of 4-bromo-3-chloro-3,3,4-trifluoro-1-butene (XIV).

The preparation of the other olefins was carried out using aqueous potassium hydroxide solutions. Yields varied from 39% for XXVIII to 71% for XX.

The Preparation of the Dienes.—The olefins, prepared as described above, were dehalogenated with zinc to give the dienes using either propanol-1 or propanol-2 as solvent. Yields were good, the lowest (64%) was obtained for XXIX. The general method is illustrated by the preparation of 1,1,2-trifluoro-1,3-butadiene.

4-Bromo-3-chloro-3,4,4-trifluorobutene-1 (XIV) (1 mole) was added dropwise to a refluxing slurry of zinc dust (2 moles) and zinc chloride (1 g.) in propanol-2 (200 ml.). The product, 1,1,2-trifluorobutadiene, was collected in a Dry Ice–acetone cooled trap as it was formed. Distillation of the crude material (110 g.) using a 42-cm. vacuum jacket column and Dry Ice–acetone cooled head resulted in 95 g. (88%) of the pure 1,1,2-trifluorobutadiene,[5] b.p. 7.8–8.0°.

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