N-Trifluoroacetyl-L-phenylalanylanilide (VII).—The acid chloride of N-trifluoroacetyl-L-phenylalanine was prepared from 264.6 mg. (0.946 mmole) of the acetylated amino acid in the usual manner. The crude acid chloride was taken up in 5 ml. of dry benzene and to the cold solution was slowly added a solution of 0.21 ml. (0.20 g., 2.4 mmoles) of aniline in 5 ml. of dry benzene. A heavy white precipitate separated. The reaction mixture was heated under reflux for one hour and the solvent was removed under reduced pressure. The solid residue was extracted with three 4-ml. portions of water, and the crude product was crystallized from 10 ml. of 70% aqueous ethanol. The white, fine, silky needles were filtered from the cold ethanolic solution, washed with two 5-ml. portions of water and dried *in vacuo;* yield 275.6 mg. (80.8%), m.p., 195.5–198.5°. A sample was recrystallized from 70% aqueous ethanol and dried at 100° *in vacuo* for analysis.

Anal. Calcd. for $C_{17}H_{15}F_3N_2O_2$: C, 60.71; H, 4.50; N, 8.33. Found: C, 60.89; H, 4.47; N, 8.10; $[\alpha]^{27.2}_{D}$ +54.3° (0.0196 g. in 5.00 ml. of 95% ethanol).

Isolation of L-Phenylalanylanilide (VIII).—To a solution of 91.1 mg. (0.271 mmole) of N-trifluoroacetyl-L-phenylalanylanilide in 5.0 ml. of 95% ethanol was added 1.0 ml. of 1 *N* sodium hydroxide. The basic solution was allowed to stand for 48 hours at room temperature and then acidified with 1 *N* hydrochloric acid. On evaporation to dryness, the solid residue was extracted with 2 ml. of dilute aqueous ammonia and the crude product was crystallized from 4 ml. of 50% aqueous ethanol; yield 37.0 mg. (56.9%), m.p. 72.6–74.2°, $[\alpha]^{25.5}_{D}$ +22.1° (0.0102 g. in 1.00 ml. of abs. ethanol); reported for L-phenylalanylanilide m.p. 72–74°, $[\alpha]^{26}_{D}$ +19°.[7]

BERKELEY, CALIFORNIA

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

Free Radical Additions Involving Fluorine Compounds. IV. The Addition of Dibromodifluoromethane to Some Fluoroölefins[1]

BY PAUL TARRANT, ALAN M. LOVELACE AND MARVIN R. LILYQUIST

RECEIVED OCTOBER 20, 1954

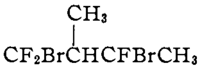
Dibromodifluoromethane has been found to react readily with fluoroölefins containing relatively few fluorine atoms to give the one-to-one addition product in the presence of benzoyl peroxide. The presence of greater number of fluorine atoms in the olefins leads to two-to-one and higher addition products. The effect of the position of the fluorine on the course of the reaction is discussed. The addition products from dibromodifluoromethane and various olefins have been converted into other fluorine-containing molecules such as olefins, dienes and cyclic compounds. In certain cases replacement of bromine by hydrogen can be carried out.

It was reported in the first paper of this series[2] that dibromodifluoromethane reacts with a variety of hydrocarbon olefins in the presence of benzoyl peroxide to give one-to-one addition products which could be converted to 1,1-difluorobutadienes. Chloroölefins were found to be unreactive toward the dibromomethane.

It seemed of interest to study the reaction of dibromodifluoromethane with fluoroölefins to determine the effect of fluorine on the course and extent of the reaction. Furthermore, should the reaction proceed satisfactorily to give simple addition products, it seemed that a convenient method of synthesis of polyfluorobutadienes could be developed. The present paper presents the results of research carried out with these objectives in view.

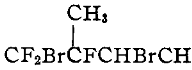
In most cases, the reaction of dibromodifluoromethane with fluoroölefins proceeded in the manner similar to that described for the hydrocarbon olefins to give one-to-one addition products. In two cases, with 2-trifluoromethylpropene and 2-H-pentafluoropropene, no reaction took place.

It appears that the addition of dibromodifluoromethane to a fluoroölefin takes place in such a manner that the difluorobromomethyl group becomes attached to the carbon of the double bond which contains the fewer number of fluorine atoms. This situation is well represented in the reaction with 2-fluorobutene-2, where the compound represented by I or II could be obtained.



$CF_2BrCH(CH_3)CFBrCH_3$

I



$CF_2BrCF(CH_3)CHBrCH_3$

II

The adduct was shown to have structure I by conversion to a methyltrifluorobutadiene by dehydrohalogenation.

Reactions with fluoroethylenes also follow the same course outlined above. For example, 1,1-difluoroethylene gave the symmetrical product $CF_2BrCH_2CF_2Br$ from which hydrogen bromide could be removed quite readily. Trifluoroethylene also gave some of the one-to-one addition product from which hydrogen bromide was removed to give the known[3] perfluoroallyl bromide. In neither case would it be possible to remove the halogen acid had the difluorobromomethyl group attacked the carbon containing two fluorine atoms.

Haszeldine[4] has shown that fluoroethylene reacts with trifluoromethyl iodide in the presence of ultraviolet radiation to give 1,1,1-tetrafluoro-3-iodopropane. Dibromodifluoromethane has been found to follow the same course with fluoroethylene to give 1,3-dibromo-1,1,3-trifluoropropane. The structure of the adduct was established by its fluorination to a bromotetrafluoropropane which gave the known 1,1,1,3-tetrafluoropropane when reduced with zinc and hydrochloric acid.

It should be noted that the use of the fluoroethylenes and 2-fluorobutene-2 gives products with dibromodifluoromethane in which the order of the free

---

(1) This work was supported under Contract DA44-109-qm-1469 with the Office of the Quartermaster General. Presented in part at the 124th Meeting of the American Chemical Society, Chicago, Ill., September, 1953.

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

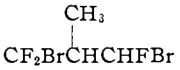
(3) A. H. Fainberg and W. T. Miller, Jr., p. 7K, Abstracts of Papers, 120th Meeting of the American Chemical Society, New York, N. Y., September, 1951.

(4) R. N. Haszeldine, *J. Chem. Soc.*, 1199 (1953).

radical intermediate which arises is not dependent upon the position of the fluorine in the olefin; thus, primary radicals of the type $CF_2BrCHXCX_2\cdot$ or $CF_2BrCX_2CHX\cdot$, where X may be hydrogen or fluorine, would result from the ethylenes and a secondary radical of the type $CF_2BrCH(CH_3)\underset{\cdot}{C}FCH_3$ or $CF_2BrCF(CH_3)\underset{\cdot}{C}HCH_3$ would be obtained from 2-fluorobutene. The results described in the preceding paragraphs therefore do not take into account the effect of different orders of free radical intermediates on the course of the reaction. This point is brought out in the reaction with 1-fluoropropylene in which the straight chain compound III was formed rather than the branched chain isomer represented by IV. It is thus evident that in

$CF_2BrCHFCHCH_3$

III



$CF_2Br\overset{\overset{CH_3}{|}}{C}HCHFBr$

IV

this case the effect of the fluorine is less pronounced than the effect of the order of the intermediate radical. However, the presence of two fluorine atoms in the 1-position of a terminal olefin is more important than the radical order as it has been shown that 1,1-difluoropropylene gives branched-chain compounds with trifluoromethyl iodide and bromotrichloromethane.[5]

A comparison of the results obtained in the ethylene series provides some interesting results. The reaction of dibromodifluoromethane with ethylene has been shown to proceed rapidly with the evolution of considerable heat.[2] The reactions with fluoroethylenes, on the other hand, proceeded smoothly and the one-to-one addition products were obtained in all cases. However, it was noted that the progressive substitution of hydrogen by fluorine gave increasing quantities of higher molecular weight products. For example, fluoroethylene gave preponderantly the simple one-to-one addition product; 1,1-difluoroethylene gave appreciable quantities of both the one-to-one adduct and product containing two olefin units for each dibromodifluoromethane molecules which reacted; and trifluoroethylene gave some simple adduct, a greater quantity of the two-to-one adduct and an even larger amount of higher molecular weight material.

From the evidence presented above it is apparent that the replacement of hydrogen by fluorine exerts a retarding effect upon the simple addition reaction. It is also evident that the isolation of the two-to-one and higher addition products is an indication that the last step in the reaction represented by 1 is retarded sufficiently to allow the competing reaction 2 to take place. With hydro-

$$CF_2BrCHXCX_2\cdot + CF_2Br_2 \longrightarrow CF_2BrCHXCX_2Br + CF_2Br\cdot \quad (1)$$

$$CF_2BrCHXCX_2\cdot + CHX{=}CX_2 \longrightarrow CF_2BrCHXCX_2CHXCHX_2\cdot \quad (2)$$

carbon olefins and those fluoroölefins which contain relatively few fluorine atoms, reaction 1 occurs so rapidly that higher adducts are not formed.

The two-to-one addition products undoubtedly are of the type $CF_2BrCHXCX_2CHXCX_2Br$. If the mechanism postulated by Kharasch[6] for peroxide-catalyzed reactions of halomethanes to olefins is accepted, it follows, for example, that the radical $CF_2BrCHFCF_2\cdot$ must be formed in the reactions with CF_2Br_2 and trifluoroethylene. It seems unlikely that such a radical would attack a second molecule of olefin in a different manner than does the bromodifluoromethyl radical.

The dehydrohalogenation of the addition products obtained from dibromodifluoromethane and the ethylenes affords a convenient method of synthesis of 3-bromo-3,3-difluoropropylenes. For example, $CF_2BrCH{=}CH_2$ was obtained from $CF_2BrCH_2CH_2Br$, $CF_2BrCH{=}CF_2$ from $CF_2BrCH_2CF_2Br$ and $CF_2BrCF{=}CF_2$ from $CF_2BrCHFCF_2Br$. Yields were good since the saturated compounds reacted with aqueous potassium hydroxide and the formation of ethers, which often results when alcoholic bases are employed for dehydrohalogenation of fluorine-containing compounds, was avoided.

The 1,3-dibromobutanes obtained by treating dibromodifluoromethane with propylenes were converted to dienes when treated with bases. Although analogous 1-chloro-3-bromobutanes, obtained from bromochlorodifluoromethane and propylenes, gave the corresponding 1-chloro-2-butene,[7] the 1,3-dibromides could not be converted to olefins of this type. For example, heating the dibromodifluoromethane–1-fluoropropylene addition product with a tertiary amine gave 1,1,2-trifluoro-1,3-butadiene, which had the same properties as the diene obtained from 2-chloro-1,4-dibromo-1,1,2-trifluorobutane.[8] Park, *et al.*,[9] have reported recently the synthesis of 1,1,2-trifluoro-1,3-butadiene by a method involving the addition of perfluorovinyl iodide to ethylene. In the present research, the isomeric 1,1,3-trifluoro-1,3-butadiene was obtained by treating the dibromodifluoromethane-2-fluoropropylene addition product with amine and 2-methyl-1,1,3-trifluoro-1,3-butadiene was obtained from the 2-fluoro-2-butene adduct. It is of some interest to note that the replacement of one hydrogen by fluorine in the 2-position of 1,1-difluoro-1,3-butadiene[10] raises the boiling point by about 5°, whereas the replacement of hydrogen in the 3-position causes an increase of 12°; the replacement of hydrogen in the 3-position of 1,1-difluoro-2-methyl-1,3-butadiene[11] increases the boiling point from 35 to 50°. Previously, Haszeldine and Steele[12] have noted that the concentration of fluorine at one end of a molecule gives lower boiling points in the fluoropropylene series.

It has been demonstrated that compounds such as 3-bromo-1-chloro-1,1-difluorobutane were reduced by refluxing with zinc and acid to the corre-

---

[5] R. N. Haszeldine, *J. Chem. Soc.*, 3565 (1953).

[6] M. S. Kharasch, O. Reinmuth and W. H. Urry, THIS JOURNAL, **69**, 1105 (1947).

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

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

[9] J. D. Park, R. J. Seffl and J. R. Lacher, p. 34M, Abstracts of Papers, 126th National Meeting, American Chemical Society, New York, N. Y., September, 1954.

[10] P. Tarrant, M. R. Lilyquist and J. A. Attaway, THIS JOURNAL, **76**, 944 (1954).

[11] P. Tarrant, J. A. Attaway and A. M. Lovelace, *ibid.*, **76**, 2343 (1954).

[12] R. N. Haszeldine and B. R. Steele, *J. Chem. Soc.*, 1592 (1953).

TABLE I

THE PROPERTIES OF THE ADDITION PRODUCTS OF FLUOROÖLEFINS AND DIBROMODIFLUOROMETHANE

Olefin	Addition product	Convn. %	B.p., °C.	Press., mm.	n^{25}_D	d^{25}_4	MR_D		Bromine, %	
							Calcd.	Found	Calcd.	Found
$CH_2{=}CHF$	CF_2BrCH_2CHFBr	34	115–116	760	1.4256	2.0875	31.58	31.47	48.8	48.2
	$CF_2Br(CH_2CHF)_2Br$	10	71.5	38	1.4560	1.8259	40.82	42.14	52.9	53.0
$CH_2{=}CF_2$	$CF_2BrCH_2CF_2Br$	28	42.5	85	1.3974	2.0943	31.18	31.22	58.4	58.1
	$CF_2Br(CH_2CF_2)_2Br$	23	54.2	14	1.4032	2.003	40.82	40.88	47.3	46.9
$CHF{=}CF_2$	$CF_2BrCHFCF_2Br$	9	35	78.5	1.3816	2.1025	31.58	32.10	54.6	54.8
	$CF_2Br(CHFCF_2)_2Br$	18	60–63	24.8	1.4237	1.9254	40.82	48.61	42.7	42.6
$CHF{=}CHCH_3$	$CF_2BrCHFCHBrCH_3$	55	56	43	1.4403	1.9438	36.20	36.43	59.2	57.4
$CH_2{=}CFCH_3$	$CF_2BrCH_2CFBrCH_3$	58	52	35	1.4346	1.9352	36.20	36.19	63.7	63.2
$CH_3CF{=}CHCH_3$	$CF_2BrCH(CH_3)CFBrCH_3$	75	65	29.5	1.4469	1.8414	40.72	40.88	56.3	56.8

sponding 1-chloro-1,1-difluoro derivative. Attempts were made to replace one bromine by hydrogen in the 1,3-dibromides by this technique but no 1-bromo-1,1-difluoroalkanes were formed; products were obtained which corresponded in properties to cyclopropane derivatives. These compounds were prepared in better yield by treating the addition compounds with zinc and propanol. In this manner, 1,1-difluoro-2,3-dimethylcyclopropane and 1,1-difluoro-2,2-dimethylcyclopropane were obtained from $CF_2BrCH(CH_3)CHBrCH_3$ and $CF_2BrCH_2CBr(CH_3)_2$, respectively. The infrared spectra of the ring compounds showed intense absorption at 9.86 μ. Slabey[13] has concluded, on the basis of a study of 34 cyclopropane derivatives, that the 9.5 to 10.0 region is most suitable for determining the presence of the cyclopropyl ring and has shown that the relatively simple compounds such as 2-cyclopropane consistently have absorption maxima at 9.82 μ.

The dibromodifluoromethane–olefin reaction products can be transformed into trifluoromethyl compounds by treatment with a fluorinating agent. For example, 1,3-dibromo-1,1-difluoropropane gave a 59.5% conversion to 3-bromo-1,1,1-trifluoropropane when heated with hydrogen fluoride in the presence of antimony pentachloride. The monobromide has been converted to the olefin, $CF_3CH{=}CH_2$, in 75% yield and reduced with zinc and acid to $CF_3CH_2CH_3$. The 1,1-difluoroethylene adduct, $CF_2BrCH_2CF_2Br$, upon treatment with antimony trichloridefluoride at 100° gave an 85% yield of 1,1,1,3,3,3-hexafluoropropane but, under milder conditions, gave 1-bromo-1,1,3,3,3-pentafluoropropane. The last compound gave 2-H-pentafluoropropylene upon dehydrohalogenation. It is interesting to note that the treatment of 3-bromo-1,1,3,3-tetrafluoropropylene with hydrogen fluoride also gave 2-H-pentafluoropropylene in 74% yield

$$CF_2{=}CHCF_2Br + HF \longrightarrow CF_2{=}CHCF_3 + HBr$$

thus demonstrating that replacement of an allylic bromine occurs rather than addition to the double bond. 1,3-Dibromo-1,1-difluorobutane also reacted readily with hydrogen fluoride and 3-bromo-1,1,1-trifluorobutane was formed.

Since the addition of dibromodifluoromethane to olefins gives good yields of adducts which can be debrominated, dehydrobrominated and fluorinated, these reactions offer a convenient method of synthesis of many fluorine-containing compounds which are not prepared readily by other methods.

Experimental[14]

Addition of Dibromodifluoromethane to Fluoroethylene.—A stainless steel autoclave was charged with 1383 g. (6.6 moles) of dibromodifluoromethane, 118 g. (2.4 moles) of fluoroethylene and 15 g. (0.06 mole) of benzoyl peroxide, heated and agitated for four hours at 100°. The bomb was then cooled in crushed ice, opened and the contents dried and fractionated. The unreacted dibromodifluoromethane (1038 g.) was stripped off and the remaining high boiling material was distilled under vacuum. Two fractions were obtained, the first of which (210 g.) was the one-to-one adduct, CF_2BrCH_2CHFBr, with the properties shown in Table I. The conversion was 32% of theory based on the fluoroethylene.

Fraction 2 (128 g.) had the properties consistent with those expected for the two-to-one addition product as an inspection of the table will indicate.

This compound has been assigned the structure $CF_2BrCH_2CHFCH_2CHFBr$ on the basis of the established mode of addition for the one-to-one adduct. The conversion was 10%.

3-Bromo-1,1,1,3-tetrafluoropropane.—The addition product (100 g.) from dibromodifluoromethane and fluoroethylene was heated in a small stainless steel autoclave to 125° for four hours with hydrogen fluoride (40 g.) and antimony pentachloride (5 g.). The vessel was cooled, opened and the contents washed with dilute hydrochloric acid and with water. Distillation gave 3-bromo-1,1,1,3-tetrafluoropropane (11 g.), b.p. 59.2–59.5°, n^{24}_D 1.3441, d^{25}_4 1.7391. *Anal.* Calcd. for $C_3H_3BrF_4$: Br, 41.0; MR_D, 23.80. Found: Br, 40.9; MR_D, 23.60.

A second run carried out at a higher temperature (170°) gave somewhat more of this compound.

1,1,1,3-Tetrafluoropropane.—The compound (24 g.) obtained above was added dropwise to a stirred mixture of zinc (32 g.) and 1.5 *N* hydrochloric acid (250 ml.) in a flask fitted with a reflux condenser connected to a trap immersed in Dry Ice. The mixture was heated on a steam-bath for four hours. The product was distilled to give 11.5 g. of 1,1,1,3-tetrafluoropropane, b.p. 28.5–30.0°, n^{25}_D 1.2765, d^{25}_4 1.2584; MR_D calcd. 16.05, MR_D found 16.12. Haszeldine[4] has reported a boiling point of 29.4° for this compound.

3-Bromo-1,3,3-trifluoropropene.—1,3-Dibromo-1,1,3-trifluoropropane (58 g., 0.22 mole) was refluxed with a solution of 112 g. of potassium hydroxide in 100 ml. of water to give 16 g. (41%) of 3-bromo-1,3,3-trifluoropropene.

Addition to 1,1-Difluoroethylene.—The stainless steel reaction vessel was charged with 1110 g. (5.2 moles) of dibromodifluoromethane, 78 g. (1.2 moles) of 1,1-difluoroethylene and 5 g. (0.02 mole) of benzoyl peroxide, rocked and heated for four hours at 100°. The autoclave was then cooled in crushed ice and the contents dried and fractionated. The excess dibromodifluoromethane (830 g.) was stripped off and the remaining high boiling material was distilled into two fractions. Fraction 1 (93 g.) contained the one-to-one adduct, 1,3-dibromo-1,1,3,3-tetrafluoropropane.

Fraction 2, obtained in a conversion of 23%, was the two-to-one adduct which has been assigned the structure $CF_2BrCH_2CF_2CH_2CF_2Br$. An additional amount of material which could not be resolved also was formed.

3-Bromo-1,1,3,3-tetrafluoropropene.—The one-to-one adduct from above (237 g., 0.86 mole) was treated with 168

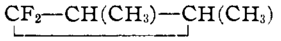
---

[13] V. A. Slabey, THIS JOURNAL, **76**, 3604 (1954).

[14] Analyses by Peninsular ChemResearch, Inc., Gainesville, Florida.

TABLE II

THE PROPERTIES OF NEW COMPOUNDS OBTAINED FROM THE ADDITION PRODUCTS OF DIBROMODIFLUOROMETHANE AND VARIOUS OLEFINS

Compound	B.p., °C.	t, °C.	n^tD	d^t_4	*MR*D Calcd.	*MR*D Found	Analyses, % Calcd.	Analyses, % Found
$CF_2{=}CF{-}CH{=}CH_2$	8.5						108.1	109.5[a]
$CF_2{=}CH{-}CF{=}CH_2$	16.9	4	1.3462	1.113	19.74	20.71	C, 44.4 H, 2.78	44.3 2.91
$CF_2{=}C(CH_3){-}CF{=}CH_2$	50	25	1.3631	1.095	24.35	24.78	C, 49.2 H, 4.12	49.8 4.26
 $CF_2{-}C(CH_3)_2{-}CH_2$	41.5–42.1	25	1.3455	0.891	23.80	24.40	C, 56.6 H, 7.55	56.8 7.60
 $CF_2{-}CH(CH_3){-}CH(CH_3)$	55–56	25	1.3521	0.926	23.80	24.71	C, 56.6 H, 7.55	56.5 7.70
$CF_2BrCH{=}CH_2$	42	25	1.3773	1.543	23.35	23.37	Br, 50.9	50.6
$CF_2BrCH{=}CHF$	41–42	25	1.3666	1.667	23.35	23.44	Br, 45.6	45.3
$CF_2BrCH{=}CF_2$	35	25	1.3463	1.747	23.35	23.35	Br, 41.3	41.7
$CF_3CH_2CF_2Br$	47.0–47.3	20	1.3228	1.784	23.82	23.85	Br, 37.5	37.7
$CF_3CH_2CHBrCH_3$	84	24	1.3740	1.521	28.13	28.60	Br, 41.8	41.3

[a] Molecular weight.

g. of potassium hydroxide in 200 ml. of water to give 113 g. (72%) of 3-bromo-1,1,3,3-tetrafluoropropene.

3-Bromo-1,1,1,3,3-pentafluoropropane.—The autoclave was charged with 1,3-dibromo-1,1,3,3-tetrafluoropropane (0.5 mole), antimony trifluoride (75 g.) and chlorine (10 g.). It was sealed, heated and rocked for 12 hours at 50°. The contents were poured over ice and HCl solution and steam distilled. The organic distillate was separated, washed with water, dried and fractionated to give 33 g. (31%) of the $CF_2BrCH_2CF_3$ b.p. 46–50°, with the properties listed in Table II, and 6.5 g. of the unreacted starting material.

1,1,1,3,3,3-Hexafluoropropane.—When the above reaction was repeated using 1,3-dibromo-1,1,3,3-tetrafluoropropane (0.5 mole), antimony trifluoride (75 g., 0.42 mole) and chlorine (30 g., 0.42 mole) at 100° for four hours, 64.5 g. (85%) of the hexafluoropropane,[15] b.p. 0.5–1.0°, was obtained.

2-H-Pentafluoropropene.—3-Bromo-1,1,1,3,3-pentafluoropropane (60 g., 0.28 mole) was added slowly to a hot solution of potassium hydroxide (60 g.) in 40 ml. of water. The product was collected in a trap immersed in Dry Ice as it was formed and fractionated to give 23 g. (62%) of $CF_3CH{=}CF_2$ b.p. −17 to −16°.

The autoclave was charged with 3-bromo-1,1,3,3-tetrafluoropropene (72 g., 0.374 mole) and hydrogen fluoride (15 g., 0.75 mole). It was sealed, heated and rocked for five hours at 150°. The gases were neutralized by a potassium hydroxide solution and collected in a trap immersed in Dry Ice. Fractionation gave 36.5 g. (74%) of $CF_3CH{=}CF_2$, b.p. −16.5°. The infrared spectrum of this material was identical with that obtained for the 2-H-pentafluoropropene prepared by the above procedure.

Addition to Trifluoroethylene.—The autoclave was loaded with 1384 g. (6.5 moles) of dibromodifluoromethane, 108 g. (1.3 moles) of trifluoroethylene and 15 g. (0.06 mole) of benzoyl peroxide, rocked and heated for four hours at 100°. The autoclave was then cooled, opened and the contents distilled to yield 1319 g. of unreacted dibromodifluoromethane and 218 g. of higher boiling material. Fractionation of this material yielded the one-to-one adduct (36 g.), $CF_2BrCHFCF_2Br$, in 9% yield. The two-to-one adduct (35 g.) obtained in an 18% conversion had the properties shown in Table I.

3-Bromoperfluoropropene-1.—Treatment of 1,3-dibromo-1,1,2,3,3-pentafluoropropane (22 g., 0.08 mole) with a solution of 56 g. of potassium hydroxide in 100 ml. of water gave 10 g. (59%) of material, b.p. 28°, n^{25}D 1.3324. This material is undoubtedly the known[3,16] perfluoroallyl bromide.

Addition to 1-Fluoropropylene.—As previously described, 1250 g. (5.9 moles) of dibromodifluoromethane, 88 g. (1.46 moles) of 1-fluoropropylene and 15 g. (0.06 mole) of benzoyl peroxide were rocked and heated for four hours at 100°. The excess reactants (777 g.) were bled off leaving 448 g. of higher boiling reactants. Distillation of this material under reduced pressure yielded 1,3-dibromo-1,1,2-trifluorobutane, $CF_2BrCHFCHBrCH_3$, whose structure was established by its conversion to 1,1,2-trifluoro-1,3-butadiene.

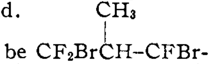
1,1,2-Trifluoro-1,3-butadiene.—1,3-Dibromo-1,1,2-trifluorobutane (194 g., 0.71 mole) was heated to 180° with 296 g. (1.6 moles) of tri-*n*-butylamine in a flask equipped with a stirrer and reflux condenser connected to traps immersed in Dry Ice. The low-boiling material (47 g.) was fractionated to give 14.5 g. (19.8%) of 1,1,2-trifluoro-1,3-butadiene with the properties listed in Table II.

Addition to 2-Fluoropropylene.—The bomb was loaded with 315 g. (1.5 moles) of dibromodifluoromethane, 22 g. (0.36 mole) of 2-fluoropropene and 5 g. (0.02 mole) of benzoyl peroxide, rocked and heated for four hours at 100°. The excess reactants (238 g.) were then bled off leaving 106 g. of higher boiling oil. Distillation of this material under reduced pressure yielded 58 g. of $CF_2BrCH_2CFBrCH_3$ with the constants shown in Table I. The conversion to one-to-one adduct was 58% based on the 2-fluoropropene.

This material must have the structure $CF_2BrCH_2CFBrCH_3$ since dehydrobromination readily yielded 1,1,3-trifluoro-1,3-butadiene.

1,1,3-Trifluoro-1,3-butadiene.—Using the procedure described above for the synthesis of 1,1,2-trifluorobutadiene, 1,3-dibromo-1,1,3-trifluorobutane (30 g., 0.11 mole) and tri-*n*-butylamine (55.8 g., 0.3 mole) gave 5 g. (42.3%) of the 1,1,3-trifluoro-1,3-butadiene.

Addition to 2-Fluoro-2-butene.—The autoclave was loaded with 393 g. (1.9 moles) of dibromodifluoromethane, 33 g. (0.44 mole) of 2-fluoro-2-butene and 5 g. (0.02 mole) of benzoyl peroxide, rocked and heated for four hours at 100°. The excess reactants (258 g.) were then bled off leaving 163 g. of light amber oil. Distillation under reduced pressure yielded the simple adduct in a 75% yield.



The structure of this material must be $CF_2Br\overset{CH_3}{\overset{|}{C}}H{-}CFBr{-}CH_3$ since it was readily dehydrobrominated to 1,1,3-trifluoro-2-methyl-1,3-butadiene.

2-Methyl-1,1,3-trifluoro-1,3-butadiene.—A mixture of 1,3-dibromo-2-methyl-1,1,3-trifluorobutane (71 g., 0.25 mole) and tri-*n*-butylamine (111 g., 0.6 mole) was treated as indicated above. Fractionation of the crude product gave 21 g. (60%) of the 2-methyl-1,1,3-trifluoro-1,3-butadiene described in Table II.

Addition to 2-Trifluoromethylpropene.—In the manner previously described 822 g. (3.9 moles) of dibromodifluoromethane, 100 g. (0.92 mole) of 2-trifluoromethylpropene and 5 g. (0.02 mole) of benzoyl peroxide were rocked and heated for four hours at 100°. After removing the excess reactants, no residue remained. Refractionation of the unreacted material yielded 124 g. of crude 2-trifluoromethylpropene, b.p. 2–8°, 738 g. of dibromodifluoromethane, b.p. 19–23°.

Addition to 2-H-Pentafluoropropene.—In the usual manner 307 g. (1.5 moles) of dibromodifluoromethane, 29 g. (0.22 mole) of 2-H-perfluoropropene and 2 g. (0.008 mole) of benzoyl peroxide were rocked and heated for four hours

---

(15) A. L. Henne and T. P. Waalkes, THIS JOURNAL, **68**, 496 (1946).

(16) W. T. Miller, Jr., private communication.

at 100°. Distillation of the contents of the bomb yielded 29 g. of unreacted 2-H-perfluoropropene.

1,1-Difluoro-2,3-dimethylcyclopropane.—A three-liter flask was charged with 325 g. (5 moles) of zinc dust, 5 g. of zinc chloride and 250 ml. of 1-propanol. To the refluxing mixture was added 710 g. (2.3 moles) of 1,3-dibromo-1,1-difluoro-2-methylbutane.[2] The material distilling from the reaction flask at 54–60° was dried and fractionated to give 66 g. (39%) of the cyclopropane with the properties described in Table II.

1,1-Difluoro-2,2-dimethylcyclopropane.—In the manner described above 133 g. (0.5 mole) of 1,3-dibromo-1,1-difluoro-3-methylbutane[2] was treated with a mixture of 65 g. (1 mole) of zinc dust, 1 g. of zinc chloride and 250 ml. of 1-propanol. Fractionation of the crude product gave 27% of the 1,1-difluoro-2,2-dimethylcyclopropane.

3-Bromo-3,3-difluoropropene.—1,3-Dibromo-1,1-difluoropropane[2] (51 g., 0.21 mole) was treated with a solution of 56 g. of potassium hydroxide in 100 ml. of water contained in a 500-ml. flask. The product distilling from the reaction mixture at 42–52° was washed, dried and fractionated giving 21 g. (63.6%) of the desired 3-bromo-3,3-difluoropropene.

3-Bromo-1,1,1-trifluoropropane.—A 500-ml. stainless steel rocking autoclave was charged with 1,3-dibromo-1,1-difluoropropane[2] (1 mole), hydrogen fluoride (3.5 moles) and antimony pentachloride (6 ml.). It was heated and rocked 18 hours at 150°. The contents were then poured onto chipped ice, neutralized with dilute sodium hydroxide solution and steam distilled. The organic layer was separated, dried and fractionated using a 45-cm. column packed with glass helices to give 100 g. (56.5%) of the desired 1,1,1-trifluoro-3-bromopropane,[17] b.p. 62–64°, $n^{22}D$ 1.3606, and 40 g. of the unreacted dibromodifluoropropane.

1,1,1-Trifluoropropene-2.—3-Bromo-1,1,1-trifluoropropane (100 g., 0.57 mole) was refluxed with a saturated solution of 75 g. of potassium hydroxide in ethanol. The product was collected in a trap immersed in Dry Ice as it formed. Fractionation using a 40-cm. vacuum jacket column gave 41 g. (74.5%) of $CF_3CH{=}CH_2$,[18] b.p. −18 to −16°.

1,1,1-Trifluoropropane.—3-Bromo-1,1,1-trifluoropropane (90 g., 0.5 mole) was refluxed with 130 g. of zinc dust in 700 ml. of 1.5 *N* HCl solution for six hours. The product was collected in a trap immersed in Dry Ice and fractionated to give 20 g. (41%) of $CF_3CH_2CH_3$,[19] b.p. −12°.

3-Bromo-1,1,1-trifluorobutane.—1,3-Dibromo-1,1-difluorobutane[2] (236 g.), hydrogen fluoride (100 g.) and antimony pentachloride (5.6 ml.) were charged into the autoclave. The clave was sealed, heated and rocked 18 hours at 135°. The contents were poured onto cracked ice, neutralized and steam distilled. The organic layer (130 g.) was separated, dried and fractionated to give 90 g. (50%) of 3-bromo-1,1,1-trifluorobutane.

1,1,1-Trifluorobutene-2.—In the manner described, 3-bromo-1,1,1-trifluorobutane (37 g., 0.194 mole) was refluxed with a saturated solution of alcoholic potassium hydroxide. The product was collected in a trap immersed in Dry Ice as it was formed. Fractionation using a 40-cm. vacuum jacket column gave 17 g. (80%) of the desired 1,1,1-trifluorobutene-2,[20] b.p. 17.7°.

Acknowledgment.—We wish to acknowledge the assistance of Mr. B. E. Gray and Mr. F. F. Norris who carried out some of the fluorination reactions,

---

[17] E. T. McBee, H. B. Hass, W. G. Toland. Jr., and A. Truchan, *Ind. Eng. Chem.*, **39**, 420 (1947).

[18] A. L. Henne and S. Kaye, THIS JOURNAL, **72**, 3369 (1950).

[19] A. L. Henne and A. M. Whaley, *ibid.*, **64**, 1157 (1942).

[20] R. N. Haszeldine, K. Leedham and B. R. Steele, *J. Chem. Soc.*, 2040 (1954).

GAINESVILLE, FLORIDA

[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY, WAYNE UNIVERSITY AND THE UNIVERSITY OF MARYLAND]

Pyrolysis of Esters. IV. Thermal Cleavage of the Cyclobutane Ring[1]

BY WILLIAM J. BAILEY,[2] CARL H. CUNOV[3] AND LOUIS NICHOLAS[4]

RECEIVED AUGUST 23, 1954

When 1,2-di-(acetoxymethyl)-cyclobutane was pyrolyzed, cleavage of the cyclobutane ring took place in two different ways to produce allyl acetate and 2-vinylbutadiene (I). Pyrolysis of the corresponding methyl carbonate ester also produced the triene I. No 1,2-dimethylenecyclobutane was isolated. The structure of the triene I was proved by comparison of its physical properties with those of an authentic sample and conversion with maleic anhydride to the known Diels–Alder adduct.

Since the pyrolysis of diesters was used very successfully for the syntheses of cyclic dienes such as 1,2-dimethylenecyclohexane,[5a] 1,2-dimethylenecyclopentane[5b] and 1,2-dimethylene-4-cyclohexene,[5c] it was of interest to extend these pyrolyses to the cyclobutane series. This pyrolysis would help determine the relative thermal stabilities of the cyclobutane ring and the ester group. If the cyclobutane ring were stable to pyrolysis, the very interesting 1,2-dimethylenecyclobutane could be prepared very conveniently.

Cyclobutane-1,2-dicarboxylic anhydride (II)[6] was reduced with lithium aluminum hydride to 1,2-dimethylolcyclobutane (III) in an 88% yield. Heating III with acetic anhydride plus acetic acid produced an 89% yield of 1,2-di-(acetoxymethyl)-cyclobutane (IV). In order to prove that no rearrangement occurred during the esterification of the glycol, the ester IV was hydrolyzed back to the glycol III. The properties of the two samples of III were identical, and a mixed melting point of the corresponding di-α-naphthylurethans showed no depression.

When the diacetate IV was pyrolyzed over glass helices at 450° under such conditions that only 30% of two molar equivalents of acetic acid was liberated, a complex mixture of products was obtained. From this mixture was isolated 3.3% of allyl acetate (V), 2% of 2-vinylbutadiene (I), 19% of 1-methylene-2-acetoxymethylcyclobutane (VI), 2% of an isomeric diene VII plus a 63% recovery of the starting material IV. Even under these comparatively mild conditions no 1,2-dimethylenecyclobutane was isolated. If more vigorous conditions were employed so that a higher percentage of acetic acid

---

[1] (a) Previous paper in this series, THIS JOURNAL, **77**, 1133 (1955). (b) Presented in part before the Michigan College Chemistry Teachers Association, Detroit, Mich., May, 1951, and the Philadelphia Organic Chemists Club, Philadelphia, Pa., February, 1954.

[2] Department of Chemistry, University of Maryland, College Park, Md.

[3] Research Corporation Fellow, Wayne University, 1948–1950.

[4] Office of Naval Research Fellow, University of Maryland, 1951–1954.

[5] (a) W. J. Bailey and H. R. Golden, THIS JOURNAL, **75**, 4780 (1953); (b) W. J. Bailey and W. R. Sorenson, *ibid.*, **76**, 5421 (1954); (c) W. J. Bailey and J. Rosenberg, *ibid.*, **77**, 73 (1955).

[6] E. R. Buchman, A. O. Reims, T. Skei and M. J. Schlatter, *ibid.*, **64**, 2696 (1952).