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

Fluoroölefins. V. The Synthesis of 1,1-Difluoro-3-methylbutadiene[1]

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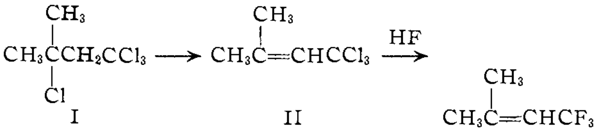
1,1,1,3-Tetrachloro-3-methylbutane has been found to be more reactive than benzotrichloride or hexachloropropylene with fluorinating agents and gives 1,1,1-trifluoro-3-chloro-3-methylbutane. A mechanism is offered to explain this unusual behavior. A method has been developed for the preparation of 1,1-difluoro-3-methylbutadiene starting with isopropyl chloride and vinylidene chloride. A number of new saturated and olefinic compounds related to 3-methylbutane and containing fluorine have been synthesized and described.

Some interest has been shown in olefins containing fluorine for use in elastomers with increased resistance to swelling by organic solvents. It has been reported that 2-fluorobutadiene polymers or copolymers are less affected by hydrocarbon solvents than butadiene[2] although no appreciable difference has been found between elastomers of 2,3-difluorobutadiene and 2-chloro-3-fluorobutadiene and elastomers from butadiene in this property.[3] In view of the conflicting reports on the effect of fluorine atoms in the butadiene molecule on its properties, it seemed desirable to prepare various dienes containing fluorine for evaluation studies. This paper presents the results of research directed toward the preparation of 1,1-difluoro-3-methylbutadiene.

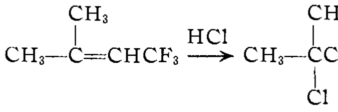
Since 1,1,1,3-tetrachloro-3-methylbutane (I) can be readily obtained from the peroxide-induced reaction of isobutylene and carbon tetrachloride, it seemed a relatively simple matter to use this material to give 1,3-dichloro-1,1-difluoro-3-methylbutane. However, it was soon discovered that the tetrachloromethylbutane, even when treated under mild conditions with hydrogen fluoride, was always converted to a trifluorochloro-3-methylbutane. This compound, upon treatment with base, gave an olefin which was oxidized to trifluoroacetic acid. It is thus evident that the product obtained in the fluorination step was 3-chloro-1,1,1-trifluoro-3-methylbutane.

Although it is possible to prepare 1,1,1-trifluoroethane by the reaction of hydrogen fluoride and trichloroethane, high temperatures are required.[4] The tetrachlorobutane (I), on the other hand, is more reactive than benzotrichloride or hexachloropropylene, which have allylic chlorine atoms. An investigation of the fluorination step has shown that 1,1,1-trichloro-3-methylbutene-2 (II) was formed at low temperature in the presence of hydrogen fluoride. This olefin also was found to give 3-chloro-1,1,1-trifluoro-3-methylbutane (IV) when treated with hydrogen fluoride. It therefore appears that the fluorination takes place as shown



$$CH_3\overset{CH_3}{\underset{Cl}{C}}CH_2CCl_3 \longrightarrow CH_3\overset{CH_3}{C}{=}CHCCl_3 \xrightarrow{HF} CH_3\overset{CH_3}{C}{=}CHCF_3$$

I II III



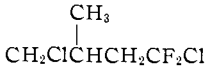
$$CH_3{-}\overset{CH_3}{C}{=}CHCF_3 \xrightarrow{HCl} CH_3{-}\overset{CH_3}{\underset{Cl}{C}}CH_2CF_3$$

IV

It has been shown that 1,1,1-trifluoropropylene accepts hydrogen chloride to form 3-chloro-1,1,1-trifluoropropane,[5] and III therefore would be expected to give IV readily because of the reinforcing effects of the methyl groups.

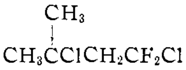
The 1,1,1-trichloro-3-methylbutene-2 was identified by hydrolysis to 3-methyl-2-butenoic acid[6] using the method of Kharasch, Reinmuth and Urry.[7]

Since the fluorination of I could not be carried out to give 1,1-difluoro-1,3-dichloro-3-methylbutane, it became necessary to prepare this compound by a different synthesis. It was found that $(CH_3)_2CHCH{=}CCl_2$[8] reacted readily with hydrogen fluoride to give good yields of $(CH_3)_2CHCH_2CF_2Cl$ and this compound could be chlorinated to give two isomeric 1,1-difluorodichloro-3-methylbutanes. Since Henne[9] has shown that the presence of two or more fluorine atoms on a carbon atom retards substitution on an adjacent methylene group, these compounds are represented by V and VI.



$$CH_2Cl\overset{CH_3}{C}HCH_2CF_2Cl$$

V



$$CH_3\overset{CH_3}{C}ClCH_2CF_2Cl$$

VI

The lower boiling compound was assigned structure VI on the basis of its reactions. It formed an olefin when treated with tributylamine under rather mild conditions; the olefin upon treatment with alcoholic potassium hydroxide gave a difluoromethylbutadiene. The infrared spectrum of this diene was identical with that of the diene[10] obtained by the dehydrohalogenation of $CF_2BrCH_2CBr(CH_3)_2$. The higher boiling dichloride was therefore assigned structure V. The chlorination of V and VI led to the formation of a single compound which must therefore have the structure $CH_2ClCCl(CH_3)CH_2CF_2Cl$. This compound was treated with zinc to give an olefin which must be $CH_2{=}C(CH_3)CH_2CF_2Cl$.

A third olefin was obtained by treatment of 1,4-dichloro-1,1-difluoro-3-methylbutane (V) with base. Since this olefin had properties different

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[1] Preceding paper in this series: THIS JOURNAL, **76**, 1624 (1954).

[2] W. E. Mochel, L. F. Salisbury, A. L. Barney, D. D. Coffman and C. J. Mighton, *Ind. Eng. Chem.*, **40**, 2285 (1948).

[3] L. B. Wakefield, *ibid.*, **43**, 2363 (1951).

[4] O. Sherer, U. S. Patent 2,146,354 (1939).

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

[6] W. von Miller, *Ann.*, **200**, 263 (1880).

[7] M. S. Kharasch, O. Reinmuth and W. H. Urry, THIS JOURNAL, **69**, 1108 (1947).

[8] Louis Schmerling, *ibid.*, **71**, 701 (1949).

[9] (a) A. L. Henne and A. M. Whaley, *ibid.*, **64**, 1157 (1942); (b) A. L. Henne and J. B. Hinkamp, *ibid.*, **67**, 1197 (1945).

[10] Paul Tarrant and A. M. Lovelace, Abstracts of Papers, 124th Meeting, American Chemical Society, Chicago, Ill., p. 35M.

TABLE I

FLUORINE DERIVATIVES OF 2-METHYLBUTANE

Compound	B.p., °C.	$n^{25}D$	d^{25}_4	MR_D Calcd.	MR_D Found	Chlorine, % Calcd.	Chlorine, % Found
$(CH_3)_2CHCH_2CFCl_2$	112–113	1.4158	1.101	34.94	36.02	44.7	43.4
$(CH_3)_2CHCH_2CF_2Cl$	77	1.3598	1.039	29.97	30.21	24.87	24.60
$(CH_3)_2CHCH_2CF_3$	37–38	1.3226	0.9788	25.00	25.27	[a]	[a]
$(CH_3)_2C{=}CHCF_3$	49.5–50.0	1.3296	1.0114	24.52	24.98	[b]	[b]
$(CH_3)_2C{=}CHCF_2Cl$	87.0	1.3960	1.083	29.49	29.92	25.22	25.30
$CH_2{=}C(CH_3)CH_2CF_2Cl$	75.1–75.6	1.3736	1.0831	29.49	29.51	25.22	24.39
$CH_2ClC(CH_3)CH{=}CF_2$	93.9	1.3881	1.1255	29.49	29.7	25.22	25.11
$CF_2{=}CHC(CH_3){=}CH_2$	35.5	1.3705	0.946	24.87	24.35	[c]	[c]
$(CH_3)_2CClCH_2CF_3$	81.0–81.2	1.3548	1.1518	29.86	30.34	22.07	21.95
$(CH_3)_2CClCH_2CF_2Cl$	56–59 (90 mm.)	1.3993	1.316	34.84	35.00	40.10	39.44
$CH_2ClCH(CH_3)CH_2CF_2Cl$	73–76 (90 mm.)	1.4055	1.237	34.84	34.92	40.10	40.01
$CH_2ClCCl(CH_3)CH_2CF_2Cl$	48–48.5 (10 mm.)	1.4311	1.3843	39.69	39.52	50.30	49.77
$(CH_3)_2CH{-}CH{=}CF_2$	27.8	1.3300	0.8711	24.83	24.82	[d]	[d]

[a] Calcd. for $C_5H_9F_3$: C, 45.7; H, 7.1. Found: C, 45.7; H, 7.3. [b] Calcd. for $C_5H_7F_3$: F, 45.9. Found: F, 46.0. [c] Calcd. for $C_5H_6F_2$: C, 57.6; H, 5.76. Found: C, 56.4; H, 5.55. [d] *Anal.* Calcd. for $C_5H_8F_2$: mol. wt., 106.1. Found: mol. wt., 109.6.

from those of $CH_2{=}C(CH_3)CH_2CF_2Cl$, it must have the structure $CH_2ClCH(CH_3)CH{=}CF_2$. This is the product which would be expected from $CH_2ClCH(CH_3)CH_2CF_2Cl$, since it has been shown that the point of attack by a base on a molecule containing fluorine is the hydrogen on a carbon adjacent to a cluster of fluorine atoms on a single carbon atom.[11]

The olefin obtained from VI is without doubt $CH_3{-}C(CH_3){=}CHCF_2Cl$ since the tertiary chlorine atom would be eliminated preferentially over the more closely held chlorine of the $-CF_2Cl$ group.

The physical properties of the various new compounds isolated are given in Table I.

Experimental

Fluorination of 1,1,1,3-Tetrachloro-3-methylbutane.—The halide (208 g.) was heated with hydrogen fluoride (38 g.) in a stainless steel rocking autoclave for four hours at 130°. The vessel was cooled, opened and the products neutralized with potassium carbonate solution and distilled. Fractionation of the dried material gave a 40% yield of 1,1,1-trifluoro-3-chloro-3-methylbutane, b.p. 79–81.2°.

Different results were obtained at lower temperatures using a somewhat different technique. One mole of $(CH_3)_2CClCH_2CCl_3$ was added to a 500-ml., three-necked, copper flask equipped with a stirrer and copper reflux condenser. The flask and contents were cooled to 5° and hydrogen fluoride (42 g.) added. The mixture was allowed to warm to 20° in 15 hours and maintained at that temperature an additional 1.5 hours. Ice was then added and the product steam distilled. Fractionation of this material gave 5 g. of $(CH_3)_2C{=}CHCCl_3$, b.p. 82° at 91 mm., $n^{29}D$ 1.4724, and 120 g. of unreacted starting material.

Anal. Calcd. for $C_5H_7Cl_3$: Cl, 61.31. Found: Cl, 60.58.

The product was found to be identical with an olefin obtained in the reaction of carbon tetrachloride and isobutylene.[12]

The olefin (20 g.) was refluxed for six hours with sodium ethoxide from 15 g. of sodium and 250 ml. of ethanol. The precipitated salts were filtered and the filtrates refluxed for 10 hours with a solution of 15 g. of potassium hydroxide in 35 ml. of water. The alcohol was removed by distillation and 200 ml. of water added and the resulting solution acidified with dilute hydrochloric acid. The brown needles which formed were recrystallized from water to give a product melting at 67–68°. The known β-methylcrotonic acid melts at 67–70°.

The Fluorination of 1,1,1-Trichloro-3-methylbutene-2.—The olefin (217 g.) was sealed in a stainless steel rocking autoclave with hydrogen fluoride (48 g.) and heated for four hours at 115°. After processing the contents as described above, 50 g. of 1,1,1-trifluoro-3-chloro-3-methylbutane, b.p. 73–83°, was obtained from which a center fraction, b.p. 79.3–80.5°, $n^{30}D$ 1.3560, gave an infrared spectrogram identical with that obtained from the product formed in the reaction of 1,1,1,3-tetrachloro-3-methylbutane and hydrogen fluoride.

1,1,1-Trifluoro-3-methylbutene-2.—3-Chloro-1,1,1-trifluoro-3-methylbutane (50 g.) was placed in a 200-ml., three-neck flask equipped with addition funnel and reflux condenser to which was attached a trap immersed in Dry Ice. Potassium hydroxide (26 g.) dissolved in 70 ml. of ethanol was added dropwise. After completion of the reaction, the products in the flask were washed and dried. Distillation gave 29 g. (79%) of 1,1,1-trifluoro-3-methylbutene-2, b.p. 49–52°.

Oxidation of 1,1,1-Trifluoro-3-methylbutene-2.—The procedure was adapted from that of Henne, *et al.*[13] The following quantities of materials were used: potassium permanganate, 136 g.; sodium hydroxide, 40 g.; water, 1 kg., and $C_5H_7F_3$, 46 g. After the completion of the oxidation, the manganese dioxide was filtered off and the filtrate distilled. The distillate was neutralized with a 20% sodium carbonate solution, evaporated to dryness, extracted with ethanol and again evaporated to dryness. The dried salt was heated with 25 ml. of sulfuric acid (96%) and ethanol and ethyl trifluoroacetate, b.p. 59–60°, $n^{25}D$ 1.3076, was obtained.

The Addition of Hydrogen Fluoride to 1,1-Dichloro-3-methylbutene-1.—Hydrogen fluoride (170 g.) and 470 g. of $(CH_3)_2CHCH{=}CCl_2$ were heated and rocked in a stainless steel autoclave for 12 hours at 110°. The contents of the clave was washed with iced water and with sodium carbonate solution and steam distilled. By refractionation, $(CH_3)_2CHCH_2CF_3$, 10 g. (2.3% yield), b.p. 35–40°; $(CH_3)_2CHCH_2CF_2Cl$, 289 g. (60.3% yield), b.p. 76–80°; and $(CH_3)_2CHCH_2CFCl_2$, 53 g. (9.8% yield), b.p. 110–115°, were obtained.

The Chlorination of 1-Chloro-1,1-difluoro-3-methylbutane.—The difluoride (360 g.) was placed in a flask equipped with a stirrer, reflux condenser and gas-inlet tube and cooled in an ice-bath. The flask was irradiated with a 140-watt Hanovia ultraviolet lamp while chlorine (160 g.) was slowly introduced. After a half-hour induction period, a moderately vigorous reaction took place. Following completion of the addition, the reaction mixture was washed and dried. From the combined products from two runs there was obtained 168 g. of $(CH_3)_2CClCH_2CF_2Cl$, b.p. 56–59° at 90 mm., and 250 g. of $CH_2ClCH(CH_3)CH_2CF_2Cl$, b.p. 73–76° at 90 mm.

The Preparation of 1,3,4-Trichloro-1,1-difluoro-3-methylbutane.—This compound was obtained from two sources.

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[11] Paul Tarrant and J. A. Young, THIS JOURNAL, **75**, 932 (1953).

[12] A. M. Lovelace, M.S. Thesis, University of Florida, August, 1952.

[13] A. L. Henne, T. Alderson and M. S. Newman, THIS JOURNAL, **67**, 918 (1945).

1,3-Dichloro-1,1-difluoro-3-methylbutane (111 g.) was placed in a 250-ml. flask equipped as described above. Chlorine (42.6 g.) was added while the flask was irradiated by ultraviolet light. The temperature was maintained at 75–80°. After addition of the chlorine, the product was neutralized with sodium carbonate solution and dried. After recovery of unreacted material, 38 g. of $CH_2ClCCl(CH_3)CH_2CF_2Cl$, b.p. 48.5–52° at 10 mm., $n^{25}{}_D$ 1.4342, $d^{25}{}_4$ 1.3906, was obtained.

1,4-Dichloro-1,1-difluoro-3-methylbutane (267.5 g.) was treated with chlorine (107 g.) as described above and 77 g. of $CH_2ClCCl(CH_3)CH_2CF_2Cl$, b.p. 48–50.5° at 10 mm., obtained. Infrared spectra of the products obtained from the isomeric dichloro starting material were identical.

4-Chloro-4,4-difluoro-2-methylbutene-1.—Powdered zinc (36 g.), zinc chloride (3 g.) and propanol-1 (75 ml.) were placed in a flask fitted with stirrer, addition funnel and a short column topped with a variable take-off head. The mixture was heated nearly to reflux temperature and a small amount of 1,3,4-trichloro-1,1-difluoro-3-methylbutane added. After reflux had begun, the remainder was added dropwise until a total amount of 45 g. was used. The olefin which resulted was removed at a temperature of 77–78°. This material was then washed, dried and refractionated. The yield of $CH_2{=}C(CH_3)CH_2CF_2Cl$, b.p. 75–75.6°, was 56% (13.5 g.).

4-Chloro-1,1-difluoro-3-methylbutene-1.—In the apparatus described above were placed 300 ml. of propanol-1 and potassium hydroxide (56 g.). To this refluxing mixture was added 1,1-difluoro-1,4-dichloro-3-methylbutane (92 g.) dropwise. The resulting olefin was removed at 85–95°. This product was then washed three times with water, dried and fractionated. The yield of $CF_2{=}CHCH(CH_3)CH_2Cl$, b.p. 93.9–94°, was 11% (8.0 g.).

1-Chloro-1,1-difluoro-3-methylbutene-2.—In the apparatus described above was placed tri-*n*-butylamine (112 g.). To the hot amine was added dropwise 1,3-dichloro-1,1-difluoro-3-methylbutane. The material refluxing at 90–110° was removed, washed, dried and fractionated yielding a fraction of 1-chloro-1,1-difluoro-3-methylbutene-2, b.p. 77–85°. This material was unstable at room temperature and split out HCl on standing.

1,1-Difluoro-3-methylbutene-1.—1,1-Difluoro-1-chloro-3-methylbutane (35 g.) was added dropwise to potassium hydroxide (28 g.) dissolved in propanol-1 (200 cc.) in a 500-cc. flask equipped with stirrer, addition funnel and six-inch column with variable take-off head. Reflux was maintained at 45°. This material was removed, washed, dried and fractionated. The 1,1-difluoro-3-methylbutene-1 (15 g.), b.p. 27.8–28.0°, was obtained in a yield of 59%.

1,1-Difluoro-3-methylbutadiene-1,3.—Tri-*n*-butylamine (112 g.) was placed in a three-neck flask equipped with addition funnel, stirrer and six-inch column with variable take-off head. The amine was heated to 180° and small portions of 1,1-difluoro-1,3-dichloro-3-methylbutane were added at intervals. The distillate, which came over at 40–50°, was washed, dried and fractionated. 1,1-Difluoro-3-methylbutadiene, b.p. 34–35.5°, was obtained in a yield of 27%.

The attempted preparation using the 1,1-difluoro-1,4-dichloro-3-methylbutane isomer failed to yield any unsaturated products when refluxed with tri-*n*-butylamine in a similar manner.

Acknowledgment.—We wish to acknowledge the interest of Dr. J. C. Montermoso of the Rubber Section of the Office of the Quartermaster General. Funds for this research were supplied under contract DA-44-109-qm-522. We wish to express our thanks to the Naugatuck Chemical Company for providing us a generous quantity of 1,1,1,3-tetrachloro-3-methylbutane.

GAINESVILLE, FLORIDA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CARNEGIE INSTITUTE OF TECHNOLOGY]

The Benzidine Rearrangement. V. Kinetics of the Rearrangement of *m*-Hydrazotoluene[1]

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Rates of rearrangement of *m*-hydrazotoluene by hydrogen chloride in 95% ethanol have been measured by means of a spectrophotometric analytical method based on an optical density *vs.* composition plot. This analytical scheme was developed because the intrinsically more accurate method used in an earlier study of the rearrangement of *o*-hydrazotoluene could not be applied to the rearrangement of *m*-hydrazotoluene, owing to the similarity of the ultraviolet absorption spectra of *m*-hydrazotoluene and *m*-tolidine. *m*-Tolidine was shown to be the only product formed in detectable amount under the imposed conditions, and its structure was verified by synthesis. The kinetics of the rearrangement of *m*-hydrazotoluene are essentially identical with those of the rearrangement of hydrazobenzene; the reaction is of the first order in *m*-hydrazotoluene concentration and of the second order in hydrogen chloride concentration under the conditions studied. The rate is subject to a positive salt effect of about the same magnitude as those which were observed in investigations of the rates of rearrangement of hydrazobenzene and of *o*-hydrazotoluene. The observed energy and entropy of activation for the process were 19.6 kcal./mole and 3.2 cal./mole-deg., respectively.

Following the completion of studies of the kinetics of the rearrangements of hydrazobenzene[2] and of *o*-hydrazotoluene[3] by hydrogen chloride in 95% ethanol, *m*-hydrazotoluene (3,3′-dimethylhydrazobenzene) was selected as the next member of a series of aromatic hydrazo compounds to be subjected to kinetic investigation in the same medium. Although the rates of transformation of *m*-hydrazotoluene in 90% ethanol have been measured and activation energies, entropies and related quantities computed,[4] the product or products of the transformation were not reported, and the effects on the rate of variations in acid concentration and in ionic strength of the solutions were not determined In the course of the work described in this article, *m*-tolidine (2,2′-dimethyl-4,4′-diaminobiphenyl) was shown to be the only detectable product from *m*-hydrazotoluene under the imposed conditions, the *m*-tolidine structure was proved by synthesis, and the dependency of the rate of rearrangement upon acid concentration and upon ionic strength were measured.

The spectrophotometric analytical method used in the two preceding investigations[2,3] has the advantage over other methods of following the rearrangement rates of aromatic hydrazo com-

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[1] From the D.Sc. Thesis by Raymond C. Odioso.

[2] R. B. Carlin, R. G. Nelb and R. C. Odioso, THIS JOURNAL, **73**, 002 (1951).

[3] R. B. Carlin and R. C. Odioso. *ibid.*, **76**, 100 (1954).

[4] L. J. Croce and J. D. Gettler, *ibid.*, **75**, 874 (1953).