[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AT THE OHIO STATE UNIVERSITY]

Fluorinated Derivatives of Propane. V

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Fluorinated derivatives of propane which are fully halogenated ($C_3F_nCl_{8-n}$), or have only one atom of hydrogen in the molecule ($C_3HF_nCl_{7-n}$) are prepared from the corresponding chlorides by means of antimony fluoride.[1] Derivatives in which all halogen atoms are linked to the same carbon, as in $CH_3CF_2CH_3$ or $CH_3CH_2CF_3$ are best prepared by the action of hydrogen fluoride on propyne[2] or on some chloro olefin.[3] For the synthesis of derivatives which bear both halogen and hydrogen atoms on the same carbon neither method works, but it has now been found that fluorination with a mixture of mercuric oxide and hydrogen fluoride[4] can be adapted to do this well.

As originally described, this method of fluorination consisted in bubbling a stream of hydrogen fluoride through a suspension of mercuric oxide in the organic bromide to be fluorinated. To adapt the procedure to organic chlorides, and to make it possible efficiently to prepare fairly low boiling compounds, the mode of operation was systematically altered until the following conditions were adopted.

A cylindrical steel vessel, made of pipe fittings, is used whose capacity is three to four times the volume of the combined reagents. One mole of mercuric oxide (red or yellow) is placed in the vessel and it is cooled with solid carbon dioxide; this quantity is sufficient to introduce two fluorine atoms in the organic molecule. Liquefied hydrogen fluoride is then delivered from a dry-ice condenser, until the increase of weight indicates the addition of ten to twelve moles. This is a very large excess, which acts as a solvent and prevents the formation of cakes of mercuric salts. At −78° the acid and the oxide do not react. Finally one or two moles of an organic polyhalide carefully cooled to −78° is added; the quantity depends on whether a difluoride or only a monofluoride is desired. The steel vessel is immediately closed by means of a pipe fitting arrangement bearing a pressure gage held in an up-side down position, and a releasing needle valve. When the vessel is strapped horizontally to a rocking machine, this arrangement makes it possible to protect the gage from acid vapors by filling it with a paraffinic oil, a precaution which is superfluous with gages made of stainless steel, but is indispensable with the common brass gages. The vessel is vigorously shaken while warming progressively. The reaction starts usually at room temperature. Depending on the nature of the polychloride treated, more or less heat is applied for varying lengths of time after the reaction has subsided; this is done by means of an electrically heated sleeve, and preferably with continued rocking. After cooling in crushed ice, the contents of the bomb are bled off through a sodium hydroxide solution until the pressure is exhausted. The contents of the vessel are then poured onto cracked ice, washed twice by decantation, then made alkaline. The organic product is separated from the precipitated mercury oxide by steam distillation or by solvent extraction.

Mercury can be recovered as metal[4] but it is preferable to recover it as yellow mercuric oxide. The crude oxide sometimes contains free metal and also occluded organic material. It is digested with aqua regia, which converts the metal to its chloride and destroys the organic matter. The solution is poured into twice its volume of water, to reduce the acid concentration. Suspended material (chiefly calcium fluoride) settles overnight, and is filtered off by suction. The clear filtrate is cooled to 10° and maintained at this temperature while mercuric oxide is being precipitated by addition of sodium hydroxide. After several washings, the oxide is filtered, dried at 110°, crushed finely and stored in brown bottles. The recovery is 85 to 90%.

$CH_2ClCCl_2CH_3$ (obtained by chlorine addition to commercial $CH_2{=}CClCH_3$) was fluorinated with great ease at room temperature, and yielded directly 51% of the difluoride $CH_2ClCF_2CH_3$, a known compound.[5] As expected, the CH_2Cl group was not affected.

$CH_2ClCCl_2CH_2Cl$ (obtained by chlorine addition to $CH_2{=}CCl{-}CH_2Cl$[6] made from commercial $CH_2ClCHClCH_2Cl$) was fluorinated at 125° for six hours and gave 80% yields of either $CH_2ClCClFCH_2Cl$ or $CH_2ClCF_2CH_2Cl$, depending on the relative amounts of the reagents. That fluorination took place on the central carbon only was demonstrated by chlorination of the difluoride in sunlight to $CCl_3CF_2CH_2Cl$ and $CCl_3CF_2CCl_3$, both of which are known.[5] In this chlorination, the first step was of necessity $CHCl_2CF_2CH_2Cl$ (see table), a new compound differing from its known isomer $CCl_3CF_2CH_3$[5]; the following steps were all known derivatives.

$CHCl_2CCl_2CH_2Cl$ (obtained by monochlorination of $CH_2ClCCl_2CH_2Cl$) underwent marked decomposition during fluorination. So little monofluoride was found that it could not be adequately isolated. The difluoride was difficult to purify, retained a sharp, disagreeable odor, and froze to a glass; all these characteristics were in sharp contrast with the behavior of $CHCl_2CF_2CH_2Cl$, and they lead to the conclusion that the difluoride was the "double monofluoride" $CHClFCClFCH_2Cl$. Admittedly a difluoride $CHCl_2CFClCH_2F$ would not be ruled out; such a formula is, however, discarded on the basis that there is no example of a $-CH_2Cl$ being fluorinated to a CH_2F group under the experimental conditions used.

$CCl_3CCl_2CH_3$[7] gave first a solid monofluoride melting about 100°, which could have been either $CCl_2FCCl_2CH_3$ or $CCl_3CFClCH_3$. The second of these isomers is known, and has properties which are very close to those of the monofluoride under investigation. A comparison between the two materials was done in a rigorously parallel way, *i. e.*, distillation from the same flask, with the same thermometer, and simultaneous determination of the melting point for the two individuals and also their mixture. The boiling point of the unknown was 134.9 to 135.1° and its melting point 99.8°. The known $CCl_3CClFCH_3$ boiled at 138.2 to 138.6° and melted at 102.4°. The mixed melt-

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(1) Henne and Ladd, THIS JOURNAL, **60**, 2491 (1938).

(2) Henne and Plueddeman, *ibid.*, **65**, 587 (1943); Grosse and Linn, *ibid.*, **64**, 2289 (1942).

(3) Henne and Plueddeman, *ibid.*, **65**, 1271 (1943); Henne and Whaley, *ibid.*, **64**, 1157 (1942); Renoll, *ibid.*, **64**, 1115 (1942).

(4) Henne, *ibid.*, **60**, 1569 (1938).

(5) Henne and Renoll, THIS JOURNAL, **59**, 2434 (1937).

(6) Henne and Haeckl, *ibid.*, **63**, 2692 (1941).

(7) $CCl_3CCl_2CH_3$ is a commercial product wrongly represented as $CHCl_2CHClCHCl$. The fact that it is a high melting solid militates against a formula with both halogens and hydrogens linked to the same carbon atoms. Further arguments were advanced by Dr. A. M. Whaley in a private communication as follows: "A solid is formed upon the chlorination of $CCl_3CH_2CH_3$, of $CHCl_2CCl_2CH_3$, and of $CCl_2{=}CHCH_3$ which is the same in all three cases and which analyzes correctly for $C_3Cl_5H_3$. $CHCl_2CCl_2CH_3$ gives only $CCl_2{=}CClCH_3$ on dehydrohalogenation; the latter accepts chlorine to form a solid which is therefore $CCl_3CCl_2CH_3$. $CCl_3CHClCH_2Cl$ was prepared by two different methods and has a boiling point of 192.5–193."

TABLE I

PHYSICAL PROPERTIES AND ANALYSES

Compound	Freezing range	Temperature, °C. F. p.	B. p. (760 mm.)	*t*	d^t_4	n^t_D	*MR*	AR_F	Chlorine, % Calcd.	Chlorine, % Found	Fluorine, % Calcd.	Fluorine, % Found
$CH_2ClCF_2CH_2Cl$	0.03	−30.04	96.69	20.0	1.4156	1.3959	25.27	0.84	47.7	47.9	25.5	25.2
$CH_2ClCClFCH_2Cl$	.1	−67.8	130.80	20.0	1.4579	1.4466	30.29	0.74	64.4	64.3	11.5	11.3
$CHCl_2CF_2CH_2Cl$	.01	−60.80	127.27	20.0	1.5446	1.4230	30.20	0.89	58.0	57.7	20.7	20.5
$CCl_3CF_2CH_2Cl$	.01	−17.13	151.18	20.0	1.6386	1.4440	35.05	0.86	65.1	65.1	17.4	17.1
$CCl_2FCF_2CH_2Cl$	.8	−79.8	109.5	20.0	1.581_4	1.396_1	30.61	1.09		[a]		
$CClF_2CF_2CH_2Cl$	.2	−75.0	68.2	20.0	....	1.3449	25.93	1.14		[a,b]		
$CCl_2FCClFCH_3$	.2	$+27._6$	97.7	30.0	1.457_2	1.400_0	30.52	1.03	$57._8$	57.0		
$CClF_2CF_2CCl_3$	.1	−92.78	113.95	20.0	1.7034	1.3966	35.86	1.18		[a]		
$CClF_2CF_2CH_3$	.1	−74.42	19.93	5.0	1.3509	1.3012	20.58	1.08	23.6	28.6		
$CCl_2FCClFCCl_3$	.5	−55	196.0	20.0	1.808_0	1.479_1	44.99	0.97	74.2	73.6		

[a] Completes and improves THIS JOURNAL, **62**, 3340 (1940). [b] Calculated on the basis of d = 1.5225, *ibid.*

ing point was 101.8°. This led to the conclusion that the new monofluoride was $CCl_2FCClFCH_3$, and that it formed a solid solution with its isomer.

The difluoride obtained next was called $CCl_2FCClFCH_3$, because it was also obtained independently from $CCl_3CClFCH_3$ and because its chlorination in sunlight yielded a perhalogenated compound $C_3F_2Cl_6$, different from the known $CCl_3CF_2CCl_3$, $CFCl_2CCl_2CFCl_2$ and $CCl_3CCl_2CClF_2$, and which, therefore, could only be $CCl_2FCClFCCl_3$.

$CCl_3CF_2CH_3$ (prepared by chlorination[5] of $CH_3CF_2CH_3$ obtained from propyne and hydrogen fluoride[2]) was fluorinated with great ease and yielded 86% of a tetrafluoride, for which the only possible formula is $CClF_2CF_2CH_3$. This tetrafluoride proved extraordinarily resistant to the action of chlorine in sunlight, but after weeks of contact it was converted to the perhalogenated derivative $CClF_2CF_2CCl_3$.

$CCl_3CF_2CH_2Cl$ (obtained as a by-product of the $CCl_3CF_2CH_3$ synthesis) proved difficult to fluorinate and a temperature of 135° maintained during six to eight hours was needed to achieve 50% yield. Under these conditions only traces of trifluoride were obtained as intermediate fractions. The tetrafluoride must be $CClF_2CF_2CH_2Cl$, because its chlorination in sunlight, which is quite easy, yielded $CClF_2CF_2CCl_3$.

Comments.—It is known that a R—CCl_2—R′ group, in which R does not represent hydrogen, is fluorinated as easily and as completely as a CCl_3R group. The present experiments indicate that as R changes from CH_3 to CH_2Cl to $CHCl_2$ to CCl_3, it first slows down the fluorination, then prevents its completion from —CClF— to —CF_2—, and finally impedes even its start from —CCl_2— to —CClF.

The easy fluorination of $CCl_3CF_2CH_3$ seems to indicate that the central —CF_2— group hinders the fluorination of the adjacent CCl_3 very little, as it merely retards the formation of a —CF_3 group. To find that the CCl_3 group in $CCl_3CF_2CH_2Cl$ is difficult to fluorinate seems, therefore, contradictory.

All compounds were carefully purified and most had a total freezing range of less than 0.1°. In all cases complete freezing curves were taken. The recorded properties are believed correct to the precision indicated in the table. As in the preceding papers, the atomic refractivity of fluorine AR_F (was computed by subtracting from the observed molecular refraction MR_D the increments for carbon (2.418), hydrogen (1.100) and chlorine (5.967).

Physical purification was accomplished by repeated distillation through an adiabatic column one meter long and 15 mm. in diameter, packed with glass helices, and fitted with a total reflux-partial take-off head. Tested with toluene and methylcyclohexane by the method of Fenske,[8] this column rated 19 plates.

The criterion of purity was, in all cases, the shape of the freezing curve, determined on samples of about 50 ml. with a calibrated resistance thermometer reading to 0.001°. The method of operation and of extrapolation of the freezing point to perfect purity was that of the Bureau of Standards.[9] The freezing range recorded in the table is that between incipient crystallization and inability further to stir the mass.

The normal boiling points were taken in a modified Cottrell apparatus[10] with a resistance thermometer and an automatic manostat regulating the pressure at 760.00 mm.

The densities were taken in pycnometers of 20-ml. capacity. The refractive indices were measured with a calibrated Abbe refractometer controlled to 0.05°

Summary

Directions are given for fluorination with a mixture of mercuric oxide and hydrogen fluoride, which make it possible to obtain yields as high as 85%. A series of polychloropropanes containing several hydrogen atoms in their molecules have been fluorinated to new derivatives whose physical properties are listed, and the latter have been chlorinated to the perhalogenated compounds.

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(8) Fenske, *Ind. Eng. Chem.*, **24**, 482 (1932).

(9) Mair, Glasgow and Rossini, *J. Research Natl. Bur. Standards*, **26**, 591 (1941).

(10) Quiggle, Tongberg and Fenske, *Ind. Eng. Chem.*, *Anal. Ed.*, **6**, 466 (1934).