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

Aliphatic Difluorides

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This paper is concerned with aliphatic compounds (from methane to heptane) which bear a CF_2 group. It studies the effect that the place of the CF_2 group has on their synthesis, their physical properties, their stability, and their behavior toward chlorine in sunlight.

Synthesis of 1,1-Difluorides.—Methylene fluoride is prepared with great ease by interacting methylene chloride and antimony fluoride.[1] Ethylidene chloride can be prepared in the same manner, but not readily, as the fluorination is complicated by extensive decomposition.[2] Propylidene fluoride cannot be prepared by this method. All attempts were fruitless because side reactions made impractical the handling of the fluorination products. The same negative results prevailed in the case of the butylidene derivative, and all efforts to fluorinate heptylidene chloride with a

chlorides, bearing both chlorine atoms in the 2,2-position, were allowed to react with antimony fluoride: the fluorination proceeded smoothly at once and quantitatively. A small amount of antimony pentachloride rendered the reaction very lively and convenient to handle, but was found not to be essential. There was no apparent sluggishness in the fluorination of the compounds of higher molecular weight, and the amount of decomposition was so small that all operations were successfully performed in glass equipment. The 2,2-difluorides of propane, butane and pentane were prepared thus, and their properties tabulated, in Table I, where the fluorine analysis is indicated for new compounds only.

The difluorides were practically odorless gases or liquids, with no apparent physiological effect. The only exception was heptylidene fluoride which

TABLE I

No.	Compounds	B. p., °C.	t	d^t_4	$n^t D$	MR_D	AR_F	%F Found	Calcd.
1	CH_2F_2	−51.6							
2	$CH_3CH_2CHF_2$	7 to 8						47	47.5
3	$CH_3(CH_2)_5CHF_2$	119.7	20	0.8959	1.37098	34.466	1.07	27	27.9
4	$CH_3CF_2CH_3$	− 0.6 to −0.2	0	.92					
5	$CH_3CF_2C_2H_5$	30.8	10	.9164	1.31862	20.504	1.02	40	40.4
6	$CH_3CF_2C_3H_7$	59.8	20	.8958	1.33570	25.012	0.96	35	35.2

fluoride of antimony failed, as no reaction occurred. In the face of these repeated failures, the fluorinating agent was changed from antimony fluoride to mercuric fluoride, or, more specifically, to a mixture of mercuric oxide and hydrogen fluoride. The new procedure, whose details are described elsewhere,[3] gave excellent results. Propylidene fluoride and heptylidene fluoride were obtained from the corresponding chlorides in better than 80% yields, without intermediate $RCHClF$ product detectable, and without apparent decomposition to ethylenic derivatives. The physical properties are recorded in Table I.

Synthesis of 2,2-Difluorides.—The synthesis of difluorides with the CF_2 group in the middle instead of at the end of the molecule was obtained in a manner distinctly different. Aliphatic di-

(1) THIS JOURNAL, **59**, 1400 (1937).
(2) *Ibid.*, **58**, 889 (1936).
(3) *Ibid.*, **60**, 1569 (1938).

had an odor distinctly akin to that of normal heptane.

Chlorination.—Subjected to complete chlorination in sunlight, four of these compounds gave rise to the new derivatives listed in Table II while the others gave known chlorides.

TABLE II

No.	Compound	F. p., °C.	% Cl	% F
12	$CCl_3CCl_2CClF_2$	50.8	74.3	13.0
14	$CCl_3CF_2CCl_3$	−12.9	74.2	13.2
15	$CCl_3CF_2C_2Cl_5$	− 2 to −1	76.2	10.3
16	$CCl_3CF_2C_3Cl_7$	10 to 15	77.9	8.1
	(extremely viscous)			

The chlorinations of methylene, ethylidene, and propylidene fluorides proceeded in an uneventful way, until all hydrogen atoms were replaced by chlorine. It was, however, noted that the chlorination of a fluorinated hydrocarbon is considerably more rapid and complete than that of the corresponding hydrocarbon, and, apparently, the

more fluorine present in the molecule, the more easy it is to perform its chlorination. For example: the chlorination of propane to octachloropropane is a very impractical task, while difluoropropane can be converted to difluorohexachloropropane without trouble. In the butane series, butane itself never could be fully chlorinated in this Laboratory, yet 2,2-difluoroöctachlorobutane was prepared successfully, and although the passage from the hexachloride to the octachloride was exceedingly slow, it was nevertheless practical. In the pentane series, all efforts to chlorinate pentane extensively resulted in complete decomposition. In contrast, 2,2-difluoropentane was chlorinated uneventfully at the start, very slowly after the introduction of eight chlorine atoms but without decomposition. To confirm this general observation it was found that the chlorination of propane derivatives containing three fluorine atoms was always very rapid and thorough, and that its end-point was easily detectable. When chlorine was passed through a trifluoride, it caused a green coloration which faded so rapidly in sunlight that it became possible to feed the chlorine at a rate such that it would be used immediately. A green color that would not fade after ten minutes in sunlight was always a sure indication that the chlorination had been quantitatively completed.

Whether the chlorination of the 1,1-difluorides proceeded in any but a random way, the present experiments cannot say; however, the following indications were obtained that the chlorination of 2,2-difluorides proceeds in an asymmetrical fashion. Chlorine affects first the methyl group adjacent to the CF_2 group, to produce high melting crystals represented by CCl_3CF_2R. In the case of the propane derivative, efforts were made to isolate $CCl_3CF_2CH_3$ as it was produced and, the yields being good, it became easy to prepare an adequately purified lot of crystals, which melted at 49°.[4] With the butane and pentane derivatives, similar crystals were formed, but too small an amount was obtained in each case for adequate purification. It was found that $CCl_3CF_2C_2H_5$ melted at about 58 to 60°, and that $CCl_3CF_2C_3H_7$ melted at about 52°. The chlorine analysis, in both cases, was correct within 1%. The crystals were wet, did not melt sharply and consequently the present data should have only the value of an indication.

(4) THIS JOURNAL, **59**, 2434 (1937).

In all cases, the completely chlorinated compounds had a much lower melting point than that of the asymmetrical trichloride. The hypothesis is advanced that the high melting point of the trichlorides might be due preponderantly to their entirely asymmetrical configuration. This idea is reinforced by a glance at the next table.

$\begin{cases} CCl_2FCCl_2F \\ CCl_3CClF_2 \end{cases}$	$24°$ $41°$	$\begin{cases} CCl_3CF_2CH_3 \\ CCl_3CF_2CCl_3 \end{cases}$	$49°$ $-12.9°$
$\begin{cases} CCl_2FCCl_2CCl_2F \\ CCl_3CCl_2CClF_2 \\ CCl_3CF_2CCl_3 \end{cases}$	$29.8°$ $50.8°$ $-12.9°$	$\begin{cases} CCl_3CF_2C_2H_5 \\ CCl_3CF_2C_2Cl_5 \end{cases}$	$58°$ (about) $- 1°$
		$\begin{cases} CCl_3CF_2C_3H_7 \\ CCl_3CF_2C_3Cl_7 \end{cases}$	$52°$ (about) $10-15°$

This constant parallelism between melting point and asymmetry is evident also in more highly fluorinated derivatives.[5]

Stability.—All the derivatives thus made proved quite stable, in spite of their very high molecular weight. Moreover, a comparison between $CCl_3CCl_2CClF_2$ and $CCl_3CF_2CCl_3$ indicated that the latter can stand temperatures of the order of magnitude of 250° better than the former, without loss of chlorine, and without developing detectable acidity. In general, asymmetrical compounds proved more resistant.

Discussion of the Fluorination.—A review of the above results and of the data reported earlier makes it possible to state that $-CX_3$ groups and $-CX_2-$ groups are swiftly and completely fluorinated by antimony fluoride, when the adjacent group or groups are not halogenated themselves. This yields fluorides represented by the formula RCF_3 or RCF_2R'. If, however, the adjacent groups bear some halogen atom, the fluorination is retarded and partly impeded, and the RCF_2X is the last stage that can be reached with antimony fluoride. When a $-CX_3$ group and a $-CX_2-$ group are adjacent, they also impede each other, and prevent complete fluorination. This is illustrated by the fact that $CHCl_2CCl_2CCl_3$ yields very rapidly $CHCl_2CCl_2CClF_2$, quite easily $CHCl_2CClFCClF_2$, where the fluorination with antimony fluoride tends to stop.

One of the objects of the present study is to learn enough about fluorination to make it possible to prepare $CH_2ClCF_2CH_2Cl$, $CClF_2CF_2CH_2Cl$, and $CClF_2CF_2CF_2Cl$, from which difluoro-, tetrafluoro-, and hexafluorocyclopropane will be made by Dr. H. B. Hass and his co-workers at Purdue University. Another object is to prepare the

(5) *Ibid.*, **60**, 2491 (1938), and article presently submitted for publication.

way for the production of large fluorinated molecules by condensation of several small fluorinated molecules.

Experimental

The preparation of dichlorides by interaction of an aldehyde or a ketone with phosphorus pentachloride was first attempted by the method previously described.[6]

However, it was promptly found that one could not generalize as to the advisability of adding the organic material to the phosphorus chloride, or vice versa, because resinification and ease of handling had to be reckoned with. The procedures finally adopted after pilot trials were as follows.

Preparation of $CH_3CCl_2C_2H_5$.—Phosphorus pentachloride (521 g.) was added in small portions to the ketone (190 g.), to give 126 g. of olefinic material and 76 g. of the desired dichloride. Resinification was small and did not interfere with the handling.

Preparation of $CH_3CCl_2C_3H_7$.—Same procedure as above, with 430 g. of phosphorus chloride and 182 g. of ketone, to obtain 72 g. of dichloride and about 150 g. of olefinic material. Not much resinification was observed, and the handling of the reaction products was not interfered with.

Preparation of $CH_3CH_2CHCl_2$.—Propionaldehyde (108 g.) was added slowly to phosphorus pentachloride (310 g.). After completion of the addition and standing overnight, the mixture was heated slowly to 100°, cooled, and poured slowly into water. This water was brought to its boiling point, which caused the organic chlorides to be steam-distilled. After decantation, drying and rectification 22 g. of olefinic chloride and 77 g. of the desired dichloride were obtained. As the latter was obtained in good purity, the following physical constants are recorded: b. p. 88.3°,

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(6) THIS JOURNAL, **59**, 2434 (1937).

$d^{20}{}_4$ 1.1321, $n^{20}D$ 1.42887, molecular refraction observed 25.73, calculated 25.78.

Preparation of $CH_3(CH_2)_2CHCl_2$.—Same procedure as above. The aldehyde (200 g.) added to the phosphorus pentachloride (416 g.) yielded 129 g. of dichloride, and a small amount of ethylenic monochloride.

Preparation of $CH_3(CH_2)_5CHCl_2$.—Commercial enanthaldehyde (127 g.) was added very slowly to cooled phosphorus chloride (250 g.). After completion of the addition and standing overnight, the mixture was progressively heated to 150°, which caused most of the phosphorus oxychloride to distil off. Then the distillation was pursued at reduced pressure, to give 81 g. of dichloride. The phosphorus oxychloride was poured slowly into water to permit the recovery of about 30 g. of organic dichloride.

Fluorinations.—They followed the procedures indicated in the articles referred to hereabove.

Summary

The differences between the fluorination of $RCHX_2$ compounds to $RCHF_2$ on the one hand, and of RCX_2R' to RCF_2R' on the other hand, are described. The following new compounds were prepared: $CH_3CH_2CHF_2$, $CH_3(CH_2)_5CHF_2$, $CH_3CF_2CH_3$, $CH_3CF_2C_2H_5$, and $CH_3CF_2C_3H_7$, together with the compounds resulting from the complete replacement of their hydrogen by chlorine. Their properties are tabulated. Directions are given to prepare 1,1-dichlorides and 2,2-dichlorides from an aldehyde or a ketone, respectively, and phosphorus pentachloride. The physical constants of $CH_3CH_2CHCl_2$ are given.

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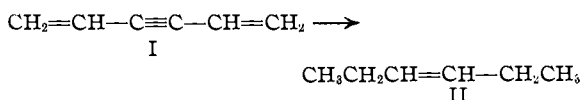

Reactions of 3-Hexene. I. Reactions with Sulfuric Acid, Halogens and Halogen Acids

BY LOUIS SPIEGLER AND J. M. TINKER

3-Hexene (II) which has been described previously by Lespieau and Wiemann[1] and Schmitt and Boord[2] recently has become available through the catalytic hydrogenation of divinylacetylene[3] (I)

$$CH_2{=}CH{-}C{\equiv}C{-}CH{=}CH_2 \longrightarrow$$
I
$$CH_3CH_2CH{=}CH{-}CH_2CH_3$$
II

The present work was undertaken with the view of studying the behavior of this relatively unknown olefin in addition reactions with sulfuric acid, halogenating agents and halogen acids.

3-Hexene combined with 85–87% sulfuric acid and hydrolysis of this mixture produced the expected 3-hexanol in 50% yields, as well as some 3,4-hexylene oxide, and a mixture of olefinic polymers $(C_6H_{12})_n$, where n has a value of two to five. Chlorine, sulfuryl chloride or phosphorus pentachloride converted 3-hexene into 3,4-dichlorohexane and some higher chlorinated products which were not identified. Dry hydrogen bro-

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(1) M. M. Lespieau and Wiemann, *Bull. soc. chim.*, [4] **45**, 627 (1929).

(2) C. G. Schmitt and C. E. Boord, THIS JOURNAL, **54**, 751–761 (1932).

(3) Du Pont Co., German Patent 649,000 (July 29, 1937).