relation of catalytic activity to adsorption of reactants. While mercury poisoning,[2,11b] heat treatment[11b] or cyanogen poisoning[3] gives a decrease in both catalytic activity and in adsorption at all pressures, carbon monoxide, when used in small amounts on either copper or nickel, while decreasing the catalytic activity, increases the low-pressure adsorption. Obviously it is the condition of activation of the adsorbed reactants rather than the extent of the adsorption which is most important in regard to catalysis.

Summary

1. Adsorption measurements have been made at 0° for hydrogen on a supported nickel catalyst poisoned with carbon monoxide.
2. A small quantity of poison causes an increase of hydrogen adsorption at all pressures up to one atmosphere.
3. A larger amount of poison gives a slight low-pressure increase and a higher-pressure decrease of adsorption.
4. Larger amounts of poison decrease the rate of adsorption.
5. An interpretation of the results has been outlined indicating a capacity for some but not all of the active centers of nickel to adsorb hydrogen as a second layer above the poison.

POUGHKEEPSIE, N. Y. RECEIVED AUGUST 20, 1937

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

Fluorinated Derivatives of Propane

BY ALBERT L. HENNE AND MARY W. RENOLL

The papers previously published by this Laboratory(1) have reported the effects of fluorine atoms in derivatives of methane and of ethane. The extension of the study to the propane series was undertaken to see whether the previously reported effects could be generalized, to learn the behavior of fluorine in newly available positions, and to observe the effect of increased distances between the various groups in the molecule.

Previous experience suggested that it would be simplest to start the research by subjecting $CCl_3CCl_2CCl_3$, $CHCl_2CCl_2CCl_3$ and $CCl_3CHClCCl_3$, respectively, to fluorination with antimony fluoride. However, after successfully replacing from one to four atoms of chlorine by the same number of fluorine atoms, it was found that the position of the fluorine atoms could not be demonstrated and therefore the publication of this phase of the work was withheld until experimental proof (recently obtained) would confirm the formulas proposed for the new compounds.

Since the monofluoropropanes are known(2) and exhibit the customary poor stability of alkyl monofluorides, and since the fluorination of a terminal $CHCl_2$ or CCl_3 group would be little more than an extension of previous work, it was decided to synthesize a difluoride with a CF_2 group in the middle of the molecule, and to do it by subjecting $CH_3CCl_2CH_3$ to fluorination with antimony fluoride. The replacement of chlorine by fluorine in a CCl_2 group isolated in the center of the molecule is a new type of reaction. It proved faster and more complete than expected. The 2,2-dichloropropane and the antimony salt react, even without catalyst, at room temperature. A small amount of bromine accelerates the reaction enormously, and is recommended, while a small amount of antimony pentachloride is frequently enough to cause the reaction to escape control. The resulting product, $CH_3CF_2CH_3$ boils about 0°, and consequently leaves the reaction field as soon as it is formed, thus allowing the reaction to proceed rapidly to completion; it carries with it from 5 to 7% of intermediate product, $CH_3CClFCH_3$.

In its general behavior, this reaction is rather similar to the fluorination of CCl_2H_2 with antimony fluoride, and that of CH_3CHBr_2 with mercuric fluoride. It differs from the fluorination of CH_3CHCl_2 with antimony fluoride because CH_3CHCl_2 undergoes much decomposition when allowed to be fluorinated so rapidly.

The point was thus made that the ease and completion of the fluorination were due to the fact that all halogen atoms were gathered on a single carbon atom, in a group isolated within the molecule; this point was confirmed by three

---

(1) THIS JOURNAL, 56, 1726 (1934); 58, 402, 404, 882, 884, 887, 889 (1936); 59, 1200, 1400 (1937).

(2) Meslans, *Compt. rend.*, 108, 352 (1889); *Ann. chim.*, [7] 1, 363 (1894).

experiments, *viz.:* the fluorination of $CH_3CClBrCH_3$ proved to be complete and rapid; while the fluorination of $CH_3CClBrCH_2Br$ and that of $CH_3CBr_2CBr_2CH_3$ were found to be troublesome operations, very similar to the fluorination of $CHCl_2CH_2Cl$ and of $CHBr_2CHBr_2$, respectively.

From the above experiments a series of new compounds were obtained, namely, $CH_3CClFCH_3$, $CH_3CF_2CH_3$, $CH_3CClFCH_2Br$, and $CH_3CF_2CH_2Br$, whose properties appear in the general table.

Effect of a Fluorinated Group on Chlorination.—The chlorination of $CH_3CClFCH_3$ in sunlight should ultimately yield $CCl_3CClFCCl_3$, a compound which was needed for identification work. However, this did not occur, as a splitting of the molecule took place; the final product was CCl_2FCCl_3, easily identified by its melting point.

The chlorination of $CH_3CF_2CH_3$ should, and does, yield ultimately $CCl_3CF_2CCl_3$. In this instance, special interest attaches to the way the chlorination proceeds; specifically, the first chlorination product can only be $CH_2ClCF_2CH_3$, but the second could be a symmetrical or an unsymmetrical dichloride (or a mixture of both), and the third could be a mixture of $CH_2ClCF_2CHCl_2$ and $CH_3CF_2CCl_3$, while the fourth chlorination product could also be a mixture. However, this does not occur. At each stage only one isomer is formed and the reaction course is found to proceed exclusively in an asymmetrical way, as follows: $CH_3CF_2CH_2Cl \longrightarrow CH_3CF_2CHCl_2 \longrightarrow CH_3CF_2CCl_3 \longrightarrow CH_2ClCF_2CCl_3 \longrightarrow CHCl_2CF_2CCl_3 \longrightarrow CCl_3CF_2CCl_3$. The chlorination has a marked tendency to stop at the $CH_3CF_2CCl_3$ stage, and as the latter is a high melting solid, while all the other stages of the chlorination (previous as well as subsequent) are liquid, it is an easy task to isolate it. The properties of these substances, all of which are new, appear in the general table. It is noteworthy that the introduction of the first and of the fourth chlorine atoms causes a rise in the boiling point of more than 50°, while the second, third, fifth and sixth chlorine atoms affect the boiling point by some 20° only.

Effect of a Fluorinated Group upon Further Fluorination.—The influence that a CF_2 group exerts upon the behavior of an adjacent group being subjected to fluorination, was studied in the case of $CH_3CF_2CCl_3$. On the basis of similarities with the ethane series, it was expected that the CCl_3 group could be fluorinated as far as a $CClF_2$ group; that the reaction would be one requiring a strong fluorinating agent, and a high temperature, that decomposition would be slight and that replacement of the hydrogen atoms would be negligible. All these predictions were substantiated. Subjected to the action of SbF_3Cl_2 at high temperature, $CH_3CF_2CCl_3$ gives only a very small amount of $CH_3CF_2CClF_2$, about 50% of $CH_3CF_2CCl_2F$, and the balance is recovered unchanged, as indicated by the fact that the melting point of the material is unaffected. The physical properties of the new compounds appear in the general table.

Results

The results of these experiments indicate that the characteristics which had been pointed out in the ethane series are still to be found in propane derivatives; more particularly, the stability and stabilizing effect of a CF_2 group have been confirmed. The facility with which an isolated CF_2 group can be produced is, however, a new fact. The physiological inertness of a compound stabilized by the presence of a CF_2 group is well illustrated by the fact that animals can be kept for hours in an atmosphere of twenty volumes of oxygen and eighty volumes of $CH_3CF_2CH_3$, and yet show no signs of discomfort, and no delayed effect.

It is known that the distance between carbon and fluorine is only 1.36 Å. in polyfluorides, against 1.42 Å. in monofluorides. Since the density of substances containing a CF_2 group is quite high and since the reactivity of the groups adjacent to the CF_2 is reduced markedly, it is a permissible speculation to wonder whether the carbon to carbon linkages have not been shortened also. This possibility is now being subjected to an experimental test.

Experimental Part

Preparation of $CH_3CCl_2CH_3$.—Acetone is allowed to drip on phosphorus pentachloride, as fast as the reaction permits—this is judged by the rate of return from a reflux condenser. The top of the condenser is connected to the bottom of a tall cylinder filled with cracked ice, so that the vapors passing through the condenser (*viz.*, $CH_3CCl{=}CH_2$, acetone and $CH_3CCl_2CH_3$) coming in contact with the ice are either dissolved or condensed; from the bottom of the ice cylinder, a mixture of ice water and organic material runs into a separatory funnel, where it forms two layers; the upper layer is a mixture of $CH_3CCl{=}CH_2$ and $CH_3CCl_2CH_3$. Yields are about 55% of dichloropropane and 45% of $CH_3CCl{=}CH_2$.

TABLE I

		M. p., °C.	B. p. (760 mm.), °C.	d^{20}_4	n^{20}_D	MRD	A. RF	Analyses, %	Found	Calcd.	Remarks
1	$CH_3CClFCH_3$		35.2	1.0072	1.35856	21.08	1.26	Cl	34.9	36.7	*d* and *n* at 10°
2	$CH_3CF_2CH_3$		−0.6 to −0.2	0.92				F	47.5	47.5	*d* at 0°
3	$CH_3CF_2CH_2Cl$		55.1	1.2023	1.3506	20.52	0.90	Cl	30.6	30.9	
4	$CH_3CF_2CHCl_2$		78.5–79.5	1.3666	1.38327	25.43	.92	Cl	47.6	47.6	
5	$CH_3CF_2CCl_3$	47–49	102					Cl	57.1	58.0	
6	$CH_2ClCF_2CCl_3$		151	1.7128	1.44421	33.94	.33	Cl		58.3	See analysis discussion
7	$CHCl_2CF_2CCl_3$		174	1.7557	1.46410	39.73	.84	Cl		70.3	
8	$CCl_3CF_2CCl_3$	−15.8	194.0–194.4	1.8136	1.48064	44.98	.96	Cl	74.2	74.3	
9	$CH_3CFClCH_2Br$		110–112	1.6475	1.45503	28.90	1.32	Cl Br	65.3	65.8	
10	$CH_3CF_2CH_2Br$		76.2–76.3	1.6102	1.38860	23.34	0.86	Br	50.3	50.3	
11	$CH_3CF_2CCl_2F$		60.0–60.3	1.4215	1.35377	25.46	.99	Cl	41.9	42.5	
12	$CCl_3CF_2CCl_2F$		152–154	1.7607	1.43887	40.38	1.10	Cl	65.4	65.6	

Preparation of $CH_3CClBrCH_3$.—The ethylenic compound is added to a saturated solution of dry hydrobromic acid in acetic acid or acetic anhydride, at 0°. The bottle is stoppered and shaken mechanically at room temperature. Every twenty-four hours the unreacted ethylenic compound is separated from the addition product (about 50% yield) and added to a fresh solution of hydrobromic acid.

Preparation of $CH_3CF_2CH_3$.—$CH_3CCl_2CH_3$ cooled to 0° is added to a 25% excess of antimony trifluoride containing 5% of bromine by weight, also cooled to 0°. The reaction vessel is connected to a metal reflux condenser filled with ice. The reaction starts promptly and is regulated by means of an ice-bath intermittently applied. At the end of the operation, the reaction vessel is heated to about 70°. The vapors passing through the condenser are caught in a water gasometer, or in a receiver cooled with solid carbon dioxide. This operation, quickly performed, yields about 85% of difluoride, and 10 to 15% of $CH_3CClFCH_3$.

Analysis.—The fluorine and chlorine contents of the gaseous and highly volatile compounds can be analyzed by decomposition over white hot silica;[3] the chlorine and bromine of the more highly chlorinated substances can be analyzed only by the Carius method and this makes it impossible to titrate the fluorine, as the glass of the tube is badly affected. All other methods cause an incomplete decomposition, and the results are from 15 to 20% of what they should be. Even the Carius method requires a whole week of continuous heating at 250 to 300° to yield quantitative results. Results which were obtained by unsatisfactory methods are not reported.

Summary

A series of new fluorinated derivatives of propane has been presented, and the physical properties have been tabulated. The influence of a CF_2 group in the middle of the molecule has been examined and its stabilizing effect has been emphasized.

---

[3] Hubbard and Henne, THIS JOURNAL, **56**, 1078 (1934).

THE MIDGLEY FOUNDATION
COLUMBUS, OHIO

RECEIVED SEPTEMBER 23, 1937

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

Researches on Pyrimidines. CLVII. The Action of Chlorine on 2,4-Diketotetrahydropyrimidines

BY TREAT B. JOHNSON AND JAMES M. SPRAGUE[1]

In connection with previous attempts to prepare 2-ethylsulfonyl-6-oxypyrimidines, the chlorination[2] of the corresponding 2-ethylmercapto compounds was carried out in methyl alcohol solution. The products formed were sulfur free, and were identified as methoxy chloropyrimidines represented by Formula IV. In the view of these results, a study has now been made of the action of chlorine upon some 2,4-diketotetrahydropyrimidines, I, in various solvents.

On treatment with chlorine in methyl alcohol suspension, the pyrimidines uracil, thymine, 4-methyluracil, 5-nitro-, 5-chloro-, and 5-bromouracil, I, were converted smoothly into the corresponding methoxychloropyrimidines, IV. When the 5-position of the diketopyrimidine I was unsubstituted (Y = H) the chlorination was accompanied by the substitution of a chlorine in this position (IV, Y = Cl). This was shown by the conversion of the methoxydichloro compounds to a 5-chloro-2,4-diketotetrahydropyrimidine (I, Y = Cl) by treatment with tin and

---

[1] Sterling Professorship of Chemistry Research Assistant, 1936–1937.

[2] Sprague and Johnson, THIS JOURNAL, **57**, 2252 (1935).