uct washed with alcohol. The cholesterol dibromide was then debrominated with sodium iodide[13] and the cholesterol recrystallized from alcohol, m. p. 146.7–147.5°.

Dihydrocholesterol.—This compound was prepared from cholesterol by the method given in "Organic Syntheses."[14] It had a melting point of 142.0–142.6°.

Dioxane.—Dioxane was purified as before.[1]

Acknowledgment.—We are grateful to Dr. C. R. Scholz of Ciba Pharmaceutical Products Inc. for supplying nine steroids and to Professor C. R. Noller of Stanford University for the three sapogenins used in this study.

Summary

The dipole moments of fourteen steroids were found to be as follows: dihydrocholesterol, 1.81; cholesterol, 1.99; androstanediol-3α,17α, 2.29; androstanediol-3β,17α, 2.99; androstanedione-3,17, 3.25; 17-methyl-Δ^5-androstenediol-3β,17α, 2.78; 17-methyl-testosterone, 4.17; 3,17-dimethyl-androstane-ol-17α, 2.06; 3,17-dimethyl-androstadiene-ol-17α, 1.81; 3,17-dimethyl-androstanediol-3,17α (Fr. A), 2.14; 3,17-dimethyl-androstanediol-3,17α (Fr. B), 2.39; tigogenin, 2.36; gitogenin, 2.64; chlorogenin, 2.67.

Five of the six compounds in the group which have a hydroxyl and one other polar group in the molecule have moments outside the values calculated for free rotation, indicating that either the 3α or the 17α positions are hindered in addition to the 3β and 17β positions which were found to be hindered in the previous work.

The angle between the ketone groups in androstane-dione-3,17 was found to be 113°. This angle is inconsistent with a flat nucleus with the ketone groups in the plane of the ring. It is consistent with a structure in which the carbon atoms are staggered, *i. e.*, the cyclohexane rings are in the chair form, the A/B, B/C and C/D rings are linked *trans*, the 3-ketone group is at an angle of 35° to a plane which can be placed through all the rings, and the 17-ketone is at an angle of 20° to this plane.

The angle between the ketone groups in Δ^4-androstenedione-3,17 is 125°. The double bond thus appreciably changes the shape of the nucleus.

The fact that 3,17-dimethyl-androstane-ol-17α has a moment about 0.2 unit higher than that of dihydrocholesterol suggests that a hydroxyl group attached to a five-membered ring has a higher moment than one attached to a six-membered ring.

Some evidence is obtained in regard to the structure of the two 3,17-dimethyl-androstanediol-3,17α isomers.

Gitogenin and chlorogenin have the same dipole moment within the experimental error.

SAN FRANCISCO, CALIFORNIA RECEIVED AUGUST 7, 1945

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[13] Schoenheimer, *J. Biol. Chem.*, **110**, 461 (1935).

[14] "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 191.

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

Directed Chlorination of Aliphatic Fluorides

BY ALBERT L. HENNE, JAMES B. HINKAMP AND WILFORD J. ZIMMERSCHIED

Preceding papers[1,2,3,4] have shown that a CF_3 group and, to a smaller extent, a CF_2 group, direct chlorination away from the hydrogen atoms linked to a carbon alpha to the fluorinated group.

Fluoroform, CHF_3, is very slowly chlorinated to CF_3Cl but the operation can be carried out in quartz when brilliant illumination is provided.[5] Methyl fluoroform, CF_3CH_3, offers a marked lag to chlorination in sunlight, but when the chlorination starts it proceeds directly to completion and yields CF_3CCl_3 uncontaminated by either CF_3CHCl_2 or CF_3CH_2Cl; when chlorination is tried on the latter it proceeds without delay and makes CF_3CCl_3 at once.[6] Trifluoropropane, $CF_3CH_2CH_3$ goes very easily and stepwise to $CF_3CH_2CCl_3$, then after much lag, but in one step, directly to $CF_3CCl_2CCl_3$.[2] These observations illustrate the fact that alpha hydrogens are protected against chlorination, though only as long as the carbon atom that bears them does not carry a halogen atom also.

More examples of the directing effect are now listed, and advantage has been taken of this property to synthesize with ease some specific compounds. The experimental operations, such as hydrogen fluoride addition, halogen exchange, substitution of hydrogen by chlorine, were performed in the manner reported in our previous papers.

Ethylidene fluoride, CHF_2CH_3, was synthesized by quantitative addition of hydrogen fluoride to vinyl fluoride, and subjected to the action of gaseous chlorine in sunlight. This chlorination yielded 70% of CF_2ClCH_3, 6% of CF_2ClCH_2Cl, but no CHF_2CH_2Cl whatever; the reaction products were actually isolated in pure state. To account for the experimental results, the following working hypothesis is proposed: (1) The CF_2 cluster is electronegative, hence the lone hydrogen

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[1] Henne and Renoll, THIS JOURNAL, **59**, 2434 (1937).

[2] Henne and Whaley, *ibid.*, **64**, 1157 (1942).

[3] Henne and Hinkamp, *ibid.*, **67**, 1195 (1945).

[4] Henne and Hinkamp, *ibid.*, **67**, 1197 (1945).

[5] Henne, *ibid.*, **59**, 1200 (1937).

[6] Henne and Renoll, *ibid.*, **58**, 887 (1936).

TABLE I

PHYSICAL PROPERTIES

Compound	F. p., °C.	B. p., °C.	t, °C.	$d^{t°}/4$	$n^{t°}/D$	*MR.*	AR_F	% Cl Calcd.	% Cl Found
$CH_3CF_2CF_2CH_3$	−52.5	16.9	0.0	1.1633	1.2915	20.42	1.04		
$CH_3CF_2CF_2CCl_3$	−90.0	123.15	20.0	1.5682	1.3908	35.35	1.12		
$CCl_3CF_2CF_2CCl_3$	+ 9.93	209.02	20.0	1.8087	1.4502	50.05	1.17	63.2	63.1
$CF_3CH_2CF_2CCl_3$	−31.88	121.56	20.0	1.6299	1.3762	35.45	1.12		
$CF_3CCl_2CF_2CCl_3$	−79.49	170.46	20.0	1.8128	1.4227	44.96	1.09	55.4	55.4
$CF_3CH_2CCl_2CCl_3$	*ca.* −22	87/30 mm.	25.0	1.7153	1.4528	44.81	1.03	62.4	62.5
$CF_3CH{=}CClCCl_3$	.....	143.21	25.0	1.6236	1.4360	39.94	1.18		
$CF_3CH{=}CClCF_3$	.....	35	25.0	1.456	1.2999	25.4	1.16	17.9	17.7
$CF_3CHClCCl_2CF_3$	.....	104	25.0	1.6968	1.3636	35.33	1.11		
$CF_3CCl{=}CClCF_3$[a]	−67.3	67.78	20.0	1.6233	1.3459	30.69	1.22	30.5	30.5
$CF_3CCl_2CCl_2CF_3$	+83 to 84	131	..	....	....	...	..	46.7	46.6

[a] *cis* and *trans* isomers mixed.

in the CHF_2 group and the three hydrogens in the CH_3 group tend to lose their electrons and become more acid. (2) From electron diffraction measurements, it is known that the nuclei of atoms linked to a fluorine cluster are pulled in, but not measurably so when they are further removed. In this case the nuclei so affected would be the hydrogen in the CHF_2 group, and the carbon in the CH_3 group. (3) It was therefore concluded that the acidity of the lone hydrogen in CHF_2 was not greatly increased because both its nucleus and its binding electrons had been simultaneously pulled in, but that the acidity of the hydrogen atoms in the CH_3 group had been much enhanced because only their binding electrons had been pulled toward the fluorinated cluster. (4) If chlorination in gaseous phase is regarded as a chain process involving atoms and free radicals, the more acid hydrogens have the least chance to come off as atoms, and they are therefore protected against chlorination.

The protective effect of a fluorinated group on the alpha hydrogen was again observed when $CH_3CF_2CF_2CH_3$ was subjected to chlorination. This tetrafluoride was made in 85% yield from $CH_3CF_2CCl_2CH_3$[4] by the nascent mercuric fluoride technique.[7] As expected, chlorine substitution was slow to start, but proceeded to yield $CH_3CF_2CF_2CCl_3$, which was easily isolated because the chlorination tended to stop at this trichloro stage; the amount of mono and dichloro compounds was not large but these intermediates were easily detected during distillation at about 72–74 and 101–103°, respectively. Continuation of the chlorination in glass, and in brilliant sunshine brought the compound directly, but very slowly to $CCl_3CF_2CF_2CCl_3$. The course of the chlorination thus paralleled that of $CH_3CF_2CH_3$.[1]

The chlorination of $CF_3CH_2CF_2CH_3$ (synthesized as shown before)[3,4] was investigated next. The CH_3 group, which is protected from only one side, was expected to be chlorinated first. In glass, with brilliant illumination, chlorination yielded a trichloride, which was formulated as $CF_3CH_2CF_2CCl_3$. As in the preceding case, the intermediates were noted at 78–80° and 100–102°, respectively. To force the chlorination to proceed further, a source of ultraviolet radiation (mercury vapor in a quartz tube) was immersed in the liquid, as previously described.[8] Under such conditions, transformation to $CF_3CCl_2CF_2CCl_3$ proceeded quantitatively; no $CF_3CHClCF_2CCl_3$ was detected.

Finally the compound $CF_3CH_2CF_3$ was synthesized[9] with the expectation that its chlorination would be exceedingly difficult, even at high temperature and in ultra-violet radiation. Experimentally, we failed to bring about any chlorination at all.

Since all examples were well in line with our previous observations, we *assumed* that resistance to chlorination indicates increased acidity of the hydrogen atoms. Advantage was taken of this assumption to devise a sequence of reactions whereby two compounds needed for a specific technical application could be made with ease; the compounds were $CF_3CCl_2CCl_2CF_3$ and $CF_3CCl{=}CClCF_3$, which could be made at the expense of each other, if one of them could be synthesized.

The starting point chosen was $CF_3CH_2CH_2CH_3$, the synthesis of which has been reported.[4] It was held that if chlorination was allowed to go to completion *in glass*, it should make $CF_3CH_2CCl_2CCl_3$ easily, and stop there. In this compound, the hydrogen atoms should be exceedingly acid, and therefore a mild treatment with an aqueous alkali should yield $CF_3CH{=}CClCCl_3$, quantitatively. In the latter compound, the CCl_3 group is allylic and therefore should be easily fluorinated,[10] to yield $CF_3CH{=}CClCF_3$. Chlorination of the latter to $CF_3CHClCCl_2CF_3$ followed by hydrogen chloride removal should yield $CF_3CCl{=}CClCF_3$, the chlorination of which yields $CF_3CCl_2CCl_2CF_3$. All operations succeeded exactly as predicted, and all of them were practically quantitative.

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[7] Henne, THIS JOURNAL, 60, 1569 (1938); Henne and Flanagan, *ibid.*, 65, 2362 (1943).

[8] Henne and Zimmerschied, *ibid.*, 67, 1235 (1945).

[9] Waalkes, Ph.D. dissertation, The Ohio State University 1945; Henne and Waalkes, paper submitted to the editor.

[10] Henne, Whaley and Stevenson, THIS JOURNAL, 63, 3478 (1941).

Definitely to prove the correctness of the sequence, the compound $CF_3CCl{=}CClCF_3$ was quantitatively oxidized by our previously reported procedure,[11] and two moles of CF_3COOH were obtained.

All compounds were purified in the manner and to the degree shown in our preceding papers, and their physical properties were measured with the accuracy denoted in the following table; they were analyzed for chlorine content at significant stages and found correct within 0.2%.

Summary

Hydrogen atoms in alpha position to a CF_2 or a CF_3 group are difficult to replace with chlorine. In order of difficulty, the following sequences were observed: $CH_3CF_2CF_2CH_3$ to $CH_3CF_2CF_2CCl_3$ to $CCl_3CF_2CF_2CCl_3$; $CF_3CH_2CF_2CH_3$ to $CF_3CH_2CF_2CCl_3$ to $CF_3CCl_2CF_2CCl_3$; $CF_3CH_2CF_3$, no chlorination observed. Advantage was taken of directed chlorination and of the acid character of hydrogen atoms alpha to a fluorinated group to synthesize $CF_3CCl{=}CClCF_3$ and $CF_3CCl_2CCl_2CF_3$ by a sequence of very efficient reactions. In CHF_2CH_3, chlorination affects the hydrogen of the CHF_2 group preferentially.

COLUMBUS, OHIO RECEIVED JULY 6, 1945

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[11] Henne, Alderson and Newman, THIS JOURNAL, **67**, 918 (1945).

[COMMUNICATION NO. 1046 FROM THE KODAK RESEARCH LABORATORIES]

Photographic Development by Ferrous Iron in Alkaline Solution

BY T. H. JAMES

In a previous paper,[1] it was shown that the rate of development of a typical photographic positive material in a very dilute ferro-oxalate solution decreases with increasing *p*H over the range 4.0 to 7.5. This decrease in rate is caused by a charge-barrier effect originating in the gelatin, and operating to oppose the approach of the negatively charged ferro-oxalate ion to the surface of the silver halide grains. In the presence of considerable amounts of neutral salt, such as potassium nitrate, the gelatin charge-barrier is largely removed, and the development rate becomes almost independent of the *p*H. The curves representing rate as a function of *p*H in the presence and absence of the added salt cross at the isoelectric point of the gelatin. From the magnitude of the salt effect and the accuracy of the development-rate determinations, it appears that the isoelectric point (in the finished film) of a gelatin sample can be determined to within 0.1 by this method, providing the isoelectric point lies below 7.5. However, a serious complication arises in the use of the ferro-oxalate developer at higher *p*H values. In the previous investigation, some data were obtained for a gelatin having an isoelectric point of about 8.0. The rate curves did cross near the isoelectric point, but the absolute values of the development rates showed a marked increase between *p*H 8 and 8.5. The present paper is concerned with the cause of this rather surprising increase in the development rate.

Experimental

Materials and Procedure.—The developers were prepared from oxygen-free component solutions, and all development operations were carried out at 20° in an atmosphere of tank nitrogen which had been freed from oxygen. The apparatus and procedure were essentially those described previously.[2] The photographic material in most of the work was a normal motion-picture positive film. The silver halide was the bromide, with only a very small addition of iodide, and the gelatin (lime-process) isoelectric point was at 4.9.

Results

The increase in rate with *p*H above 8.0 proved to be just as great with the photographic material prepared from lime-process gelatin as with that prepared from acid-process gelatin (isoelectric point 8.0). However, the rate at a given *p*H, and indeed the character of the development curve, varied markedly with the concentration of oxalate. The dependence of rate upon oxalate concentration proved to be just the opposite from that found in more acid solution. Figure 1 illustrates some typical results. All developing solutions contain 0.01 *M* ferrous salt (added as sulfate) and 0.667 *M* potassium nitrate. The latter was added to minimize the gelatin charge-barrier. The dotted curves represent data obtained at *p*H 6.0; the solid curves, data obtained at *p*H 8.3.

At *p*H 6.0, a decrease in the oxalate concentration (below 0.2 *M*) is accompanied by a decrease in the development rate. Only a very faint image developed after three hours when the solution contained only 0.02 *M* oxalate (data are not shown for this particular solution). The general shape of the development curves, however, was not altered appreciably by the change in oxalate concentration.

At *p*H 8.3, the situation is reversed. The development rate *increases* with decreasing oxalate concentration, and the character of the development curve undergoes a significant change. At a

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[1] T. H. James, *J. Chem. Physics*, **12**, 453 (1944).

[2] T. H. James, *J. Phys. Chem.*, **43**, 701 (1939).