[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

The Directing Influence of Substituents on the Chlorination of Halogenated Ethanes and Propanes[1]

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A study has been made of the chlorination under various conditions of a series of highly halogenated alkanes. It has been found that these chlorinations were for the most part highly directed; and that this orientation could readily be predicted by means of the heretofore neglected London dispersion effect, which in turn is conveniently measured by the known atomic refractivities of the halogens. The relation between structure and the reactivities of specific hydrogen atoms has been discussed, and a number of new and interesting halo-hydrocarbons have been prepared and characterized.

During the progress of recent studies in this Laboratory dealing with the direct fluorination of trichloroethylene[3] and of $CHCl{=}CCl{-}CHF_2$,[4] we became interested in the chlorination of a series of halogenated ethanes and propanes, with the idea of accounting more clearly than has been possible heretofore for the influences which frequently direct the entering halogen atom toward specific parts of the respective molecules. We have, therefore, studied the vapor phase chlorination of $CHFCl–CHCl_2$, $CHFCl–CH_2Cl$, $CHF_2–CH_2Cl$, $CHCl_2–CCl_2–CHF_2$ and $CHClBr–CClBr–CHF_2$; the last two having been prepared by the addition of chlorine and bromine, respectively, to the propene $CHCl{=}CCl{-}CHF_2$. Considering only the monochlorinated portions, the first of these compounds yielded the expected isomers $CHFCl–CCl_3$ and $CFCl_2–CHCl_2$ in the ratio of 1:1, while the second gave $CFCl_2–CH_2Cl$ and $CHFCl–CHCl_2$ in the ratio of 1:1.7 (calcd. 1:2); indicating that the attack of the chlorine atoms had been very nearly a statistical one in these cases. However, the third haloethane formed $CHF_2–CHCl_2$ and $CF_2Cl–CH_2Cl$ in the ratio of 4:1, showing that in this instance the chlorination was strongly oriented in favor of the $–CH_2Cl$ group. Finally the two halopropanes yielded exclusively $CCl_3–CCl_2–CHF_2$ and $CCl_2Br–CClBr–CHF_2$, respectively, showing that here the chlorinations had been completely directed toward the groups bearing halogen atoms other than fluorine.

Such directed chlorinations have been considered by Ash and Brown[5] to be largely due to the ordinary inductive effect, or else to the relative stabilities of the respective free radicals involved in the reactions. Also Henne, *et al.*,[6] found that the chlorination of $CH_3–CHF_2$ yielded mostly $CH_3–CF_2Cl$, but no $CH_2Cl–CHF_2$. They believed that the hydrogen atoms on the α-carbon atom were rendered more acidic by the inductive effect, and were therefore protected against attack by chlorine atoms; while in the $–CHF_2$ group both the hydrogen nucleus and its binding electrons would be drawn toward the fluorine so that this hydrogen should not be thus protected. However, since the chlorination of $CH_3–CF_3$ to give $CCl_3–CF_3$, while difficult at the outset, could not be stopped at the intermediate stages, it appeared that an α-carbon atom which also bore a chlorine atom was no longer protected as before.

Upon consideration it was clear that the results obtained in the present work could not be accounted for satisfactorily by any of these theories, although such influences were doubtless operative to some extent. It now appears very probable that another and perhaps determining influence, namely, the London dispersion effect,[7] must also be taken into account. In essence this effect means the attractive van der Waals interaction between atoms which results when periodic transient dipoles in one atom induce similar dipoles in phase with themselves in another. These forces are proportional to the polarizabilities and hence to the atomic refractions of the respective atoms, and the latter values are known for the several halogens. Obviously for a chlorination to take place, the attacking chlorine atom must approach the group to be chlorinated to within a sufficiently short distance, and this approach will naturally be oriented largely by the attractive forces due to the dispersion effect. For example, in the chlorination of $CHF_2–CHCl_2$ where the atomic refractivities of fluorine and chlorine are approximately 1.1 and 6.0, respectively, the attacking atom should be attracted to the $–CHCl_2$ group, and the product should be almost exclusively $CHF_2–CCl_3$ as has been found to be the case by Henne and Ladd.[8] It should be pointed out that if the inductive effect, rather than the dispersion effect were predominant, then the product should have been $CF_2Cl–CHCl_2$, since the $>CF_2$ group is a stronger α-hydrogen deactivator than the $>CCl_2$ group; unless, of course, an isolated inductive effect within the $–CHF_2$ group itself should prove strong enough to protect it against chlorination, even though the same group in $CH_3–CHF_2$ does not appear to be thus protected.[6] It would also be expected from the dispersion effect that the progressive chlorination of such compounds as CH_3CH_2-CF_2CH_3 and $CH_3CH_2CH_2CF_3$ should lead to the accumulation of chlorine atoms on the same carbon atom, which has been reported and specifically emphasized by Henne and Hinkamp.[9]

If the chlorinations reported here are considered as being oriented entirely according to the dispersion theory, even though other forces must operate to some extent, it would be predicted that CHFCl–

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(3) Hauptschein and Bigelow, THIS JOURNAL, **72**, 3423 (1950).

(4) Hauptschein and Bigelow, *ibid.*, **73**, 1428 (1951).

(5) Ash and Brown, *Record of Chem. Progress* (*Kresge-Hooker Sci. Lib.*), **9**, 81 (1948).

(6) Henne, Hinkamp and Zimmerschied, THIS JOURNAL, **67**, 1906 (1945).

(7) London, *Trans. Faraday Soc.*, **33**, 8 (1937).

(8) Henne and Ladd, THIS JOURNAL, **58**, 402 (1936).

(9) Henne and Hinkamp, *ibid.*, **67**, 1194, 1197 (1945).

$CHCl_2$ should yield somewhat more $CHFCl{-}CCl_3$ than $CFCl_2{-}CHCl_2$ although the attack should be much less directed than in the case of $CHF_2{-}CHCl_2$ mentioned above, where the polarizabilities of the two groups are much more distinctly different. Similarly, $CHFCl{-}CH_2Cl$ should give statistical amounts of $CHFCl{-}CHCl_2$ and $CFCl_2{-}CH_2Cl$, depending upon the number of hydrogen atoms available on the respective carbon atoms. Actually, the reaction took place in approximately random fashion in both cases.[10] On the other hand, it would be predicted that $CHF_2{-}CH_2Cl$ should yield several times as much $CHF_2{-}CHCl_2$ as $CF_2Cl{-}CH_2Cl$, while actually these compounds were produced in the ratio of 4:1, which is twice the statistical ratio. In the chlorination of the halopropanes the results were even more definite. The compound $CHCl_2{-}CCl_2{-}CHF_2$ which is in a sense a homolog of $CHCl_2{-}CHF_2$, would be expected to yield largely $CCl_3{-}CCl_2{-}CHF_2$; while $CHClBr{-}CClBr{-}CHF_2$, where the atomic refractivity of bromine is 8.9, should produce $CCl_2Br{-}CClBr{-}CHF_2$ almost entirely. Actually the predicted products were formed exclusively in both cases, and in the second instance it was clear that the attractive forces due to the large polarizability of the bromine atom more than offset the steric hindrance involved, which might have been expected to orient the chlorine atoms toward the $-CHF_2$ group. Furthermore, the observation by Henne previously referred to,[6] that carbon atoms alpha to a fluorinated cluster are protected against chlorination only so long as they do not themselves carry chlorine atoms, may be explained effectively in the same way. The preparation, chlorination and dehydrohalogenation of $CHCl_2{-}CCl_2{-}CHF_2$ were carried out independently by us,[1] and by Davis and Whaley,[11] who have described the same reactions and noted the selectivity in the chlorination, although they did not present any theoretical explanation for it.

The above considerations make it clear that in the chlorination of simple halo-hydrocarbons where each atom bears at least one halogen atom, the preferential reactivities of specific hydrogen atoms, while influenced by various factors, would seem to be determined to the greatest extent by the London dispersion effect, which in turn controls the orientation of the approaching chlorine atoms. Since this effect is measured approximately by the known atomic refractivities of the halogens, it provides a convenient means for predicting the course which such chlorinations may take. This method seems to have been neglected heretofore by investigators in this active field of research.

Experimental

Chlorination of $CHFCl{-}CHCl_2$.—The commercial sample[12] was rectified, and a central cut used, b.p. 102.2–102.6°, $n^{20}{}_D$ 1.4390, $n^{17}{}_D$ 1.4405 (known[13] b.p. 102°, $n^{17}{}_D$ 1.5492). The previously reported refractive index is incorrect since the compound was actually made by the monofluorination of $CHCl_2{-}CHCl_2$ with SbF_3, and also prepared by the chlorination of $CHFCl{-}CH_2Cl$ (see below), so that there can be no doubt as to its structure.

A 50-g. sample of the pure $CHFCl{-}CHCl_2$ was chlorinated in the vapor phase, using a slightly modified Muskat chlorinator[14] illuminated by a 200 watt lamp for 18 hr., while the temperature of the boiling sample rose from 104–117°; after which the product was washed with 5% KOH solution, dried over anhydrous $MgSO_4$, and finally rectified mostly in a Podbielniak Hyper-Cal column. There were recovered, unreacted $CHFCl{-}CHCl_2$, b.p. 102–105° (19%); $CHFCl{-}CCl_3$ + $CFCl_2{-}CHCl_2$, b.p. 115–117° (58%); and $CFCl_2{-}CCl_3$, b.p. 134–136° (12%), based by weight on the washed and dried sample. Successive fractions of a 15-g. central cut, b.p. 116°, f.p. −104°, had $n^{20}{}_D$ 1.4506–1.4508; while the reported values[13] are $CHFCl{-}CCl_3$, b.p. 116.7°, f.p. −95.4°, $n^{20}{}_D$ 1.4525 and $CFCl_2{-}CHCl_2$, b.p. 116.6, f.p. −82.6°, $n^{20}{}_D$ 1.4487. The results show that the monochlorinated product almost certainly consisted of a nearly equimolecular mixture of the two inseparable isomers. Attempts to chlorinate $CHFCl{-}CHCl_2$ in the liquid phase yielded essentially only unreacted sample or $CFCl_2{-}CCl_3$.

Chlorination of $CHFCl{-}CH_2Cl$.—The commercial sample[12] was rectified and a central cut used, b.p. 73.0–73.5°, $n^{20}{}_D$ 1.4110 (known[13] b.p. 73.9°, $n^{20}{}_D$ 1.4113). A 75-g. portion was chlorinated as before using the modified Muskat chlorinator for 12 hr., while the temperature of the boiling sample rose from 76–93°; after which the product was first distilled through a Vigreux column and finally rectified in the Podbielniak still using 10 cc. of $CHCl_2{-}CCl_2{-}CHF_2$, b.p. 147°, as a chaser. There were recovered, unreacted $CHFCl{-}CH_2Cl$, b.p. 73–74° (18%); $CFCl_2{-}CH_2Cl$, b.p. 87–89°, central cut, b.p. 88.5°, $n^{20}{}_D$ 1.4250 (23%); $CHFCl{-}CHCl_2$, b.p. 101–103°, central cut, b.p. 101.5°, $n^{20}{}_D$ 1.4390 (39%); and $CHFCl{-}CCl_3$ and/or $CFCl_2{-}CHCl_2$, b.p. near 115° (about 6%). The known values[13] for $CFCl_2{-}CH_2Cl$ are b.p. 88.8°, $n^{20}{}_D$ 1.4248; and the others are given above. Here the monochlorinated products which were separated were formed in the ratio of 23:39, or 1:1.7 by weight.

Chlorination of $CHF_2{-}CH_2Cl$.—The commercial sample[12] was rectified and a central cut used, b.p. 34.4–35.0° (known[13] b.p. 35.1°). A 20-ml. portion was chlorinated as before using the modified Muskat chlorinator, in this case provided with an additional solid CO_2–acetone condenser, for 8 hr., while the temperature of the boiling sample rose from 36–59°; after which the product was washed with 5% KOH solution, dried over anhydrous $MgSO_4$, and finally rectified in the Podbielniak still. There were recovered $CHF_2{-}CHCl_2$, b.p. 58–60° (known[13] b.p. 60°), and $CF_2Cl{-}CH_2Cl$, b.p. 45–47° (known[13] b.p. 46.8°), in the ratio of 4:1 by weight, together with small amounts of $CHF_2{-}CCl_3$ and/or $CF_2Cl{-}CHCl_2$, and unreacted sample. It is thus apparent that the chlorination was directed to a much greater extent toward the $-CH_2Cl$ group.

The Preparation, Chlorination and Dehydrochlorination of $CHCl_2{-}CCl_2{-}CHF_2$.—These operations, starting from $CHCl{=}CCl{-}CHF_2$, b.p. 89.6–90° (known[4] b.p. 90°), and carried out under many different conditions, readily yielded the adduct $CHCl_2{-}CCl_2{-}CHF_2$, b.p. 147.5°, f.p. −59° (cooling curve), $n^{20}{}_D$ 1.4485; the halopropane $CCl_3{-}CCl_2{-}CHF_2$, b.p. 174°, m.p. 139–140°; and the olefin $CCl_2{=}CCl{-}CHF_2$, b.p. 113–115°.

Anal.[15] Calcd. for $C_3H_2F_2Cl_4$: Cl, 65.1; mol. wt., 218. Found: Cl, 65.4; mol. wt. (Victor Meyer), 218.

Anal. Calcd. for $C_3HF_2Cl_5$: Cl, 70.26; mol. wt., 252. Found: Cl, 70.0; mol. wt. (in benzene), 249, 254.

No $CHCl_2{-}CCl_2{-}CF_2Cl$ was formed in any case. These results are essentially similar to those found independently[11] by Davis and Whaley.

It is also of interest that the vapor phase chlorination of the olefin, $CHCl{=}CCl{-}CHF_2$ did not yield any $CHCl{=}CCl{-}CF_2Cl$ (b.p. 97°[16]) by substitution in the allylic posi-

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(10) This result does not necessarily mean that in the molecule $CHFCl{-}CHCl_2$ no directional effects exist at all, but it does indicate that the energy level at which the experiment was conducted may have been too high for any selectivity to be evident. Perhaps, if the chlorination could be conducted in the vapor phase at low temperature, either at reduced pressure or in the presence of a diluent, then differences in activation energies might have become important and some selectivity have been observed.

(11) Davis and Whaley, THIS JOURNAL, **72**, 4737 (1950).

(12) Furnished by the Columbia Organic Chemicals Co., Columbia, S. C.

(13) "Organic Reactions," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1944, p. 76.

(14) Muskat and Northrup, THIS JOURNAL, **52**, 4043 (1930).

(15) The analyses in this paper were carried out by Mrs. Alfred R Gilbert and Miss Louise Gurney of this Laboratory.

(16) Whaley and Davis, THIS JOURNAL, **70**, 1026 (1948).

tion. Finally, the pentachloride CCl_3–CCl_2–CHF_2, on dechlorination in the usual way in alcohol solution with zinc dust, readily yielded the olefin CCl_2=CCl—CHF_2, b.p. 113–115°. An accumulated sample gave a central cut, b.p. 114.8°, $n^{20}D$ 1.4456 (known[16] b.p. 114.4°, $n^{20}D$ 1.4452).

Additive Bromination of CHCl=CCl—CHF_2.—A 50-ml. sample of the olefin was placed in a flask equipped with a dropping funnel containing bromine, a reflux condenser, and illuminated by a 200 watt lamp at a distance of 1 inch. The bromine was added intermittently, as the resulting red color disappeared, for 16 hr., after which the product was washed with alkaline-sulfite solution, dried over anhydrous $MgSO_4$ and distilled through a 25-cm. Vigreux column under reduced pressure. About 90% of it came over from 85–88° at 24 mm.; and this, on redistillation, yielded pure CHClBr–CClBr–CHF_2, b.p. 87° at 24 mm., f.p. −45° (cooling curve), $n^{20}D$ 1.5078.

Anal. Calcd. for $C_3H_2F_2Cl_2Br_2$: F, 12.4. Found: F, 12.5, 12.6.

Chlorination of CHClBr–CClBr–CHF_2.—This reaction was carried out by bubbling chlorine through the liquid bromine adduct in a flask equipped with a reflux condenser and illuminated by a 200-watt lamp at a distance of 1 inch. After a 3-hr. induction period, the slow chlorination began, which displaced practically no bromine, and was apparently complete when all the sample had been converted into a white crystalline solid. This product decomposed on heating to 100°, but was shown to consist essentially of CCl_2-Br–CClBr–CHF_2 by the debromination of a 35-g. sample in alcohol solution with zinc dust in the usual way. The product was poured into water, extracted with CH_2Cl_2, dried with anhydrous $MgSO_4$ and distilled through a 10-cm. Vigreux column. There was obtained 7.4 g. of CCl_2=CCl–CHF_2, b.p. 112–115°, central cut, b.p. 114°, $n^{20}D$ 1.4458. About 10% of the product was CHCl=CCl–CHF_2, b.p. 89–92°, indicating that the crude dibromide must have been contaminated with some CHClBr–CClBr–CHF_2.

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The Polymorphism of *n*-Hexadecanol and *n*-Octadecanol

BY D. G. KOLP AND E. S. LUTTON

The polymorphism of the fatty alcohols, *n*-hexadecanol and *n*-octadecanol, has been studied by X-ray diffraction and thermal methods. Three forms corresponding to those indicated by dielectric constant data of Hoffman and Smyth have been found. The alpha form appears from the melt at the f.p. and exists as a metastable form in a narrow temperature range near the m.p. In this temperature range gradual transformation to the stable beta form occurs. Cooling the alpha form causes abrupt transformation to the sub alpha form, which also changes gradually to beta on aging. Only one m.p. has been found for each of the alcohols studied.

Introduction

The occurrence of polymorphism in *n*-hexadecanol and *n*-octadecanol has been demonstrated by thermal curves,[1–3] X-ray diffraction[4–7] and dielectric constant studies.[8–10]

Whereas the thermal studies and X-ray diffraction work uncovered two forms (which do not seem to be the same two in all cases), dielectric constant data of Hoffman and Smyth[10] clearly indicate the existence of three solid forms of *n*-octadecanol. (*n*-Hexadecanol was not considered experimentally by them but by Baker and Smyth[8] who found two forms.) It is the purpose of this paper to clarify knowledge of the three forms of both *n*-hexadecanol and *n*-octadecanol by correlated diffraction and thermal data.

In this work, the names "alpha," "sub alpha" and "beta" have been adopted for the alcohol form first appearing from the melt, the form obtained on rapid chilling to room temperature, and the stable form obtained on aging, respectively. These names are in keeping with previous long chain alcohol nomenclature or are chosen by analogy with nomenclature used previously for certain other long chain compounds.

Experimental

Preparation of Compounds.—The *n*-hexadecanol and *n*-octadecanol used in this work were prepared by sodium reduction of natural fats, followed by distillation to separate the various homologous alcohols present. The resulting materials were crystallized from 10 volumes of petroleum ether. Crystallization was repeated to constant f.p.

Thermal Conditions for Obtaining Forms.—The following outline gives the thermal conditions under which each of the three forms was obtained,

A. **Alpha Form .**—(1) Melted; cooled to 2° below f,p.; X-rayed at this temperature. (2) Warmed sub alpha form to 2° below f.p.; X-rayed at this temperature,

B. **Sub alpha Form.**—(1) Chilled alpha form below transition temperature; X-rayed at room temperature,

C. **Beta Form.**—(1) Crystallized slowly from ethanol or petroleum ether; X-rayed at room temperature. (2) Stored alpha form 2 days at 2° below the f.p.; X-rayed at room temperature. (3) Stored sub-alpha form 1 day at 38° X-rayed at room temperature, (4) Stored beta 30 days at room temperature; X-rayed at room temperature,

Melting, Freezing and Transformation Points.—The m.p.'s reported below were obtained by raising the temperature of the sample (contained in a thin-walled glass capillary about 1 mm. in diameter), 0.5° per minute. M.p.'s were also determined by the thrust-in technique described by Lutton and Jackson.[11]

Freezing-points were obtained on 3-g. samples allowed to cool in a doubly air-jacketed apparatus placed at room temperature.

The transformation points of the alcohols were determined from time–temperature cooling curves (details described later), run very slowly with small temperature gradient between sample and surroundings.

The melting, freezing and transformation points found are 49.7° (50°[12]), 49.1° (49.3°[12]) and 43.8° (45.0°[2]), respectively, for *n*-hexadecanol and 58.6° (58.5°[12]), 57.9° (57.9°[12]) and 54.7° (53,6°[2]), respectively, for *n*-octadecanol.

X-Ray Diffraction Powder Patterns.—X-Ray diffraction powder patterns were obtained on samples solidified in thin-walled glass capillaries under various conditions, and on solvent-crystallized samples ground with mortar and pestle and pressed into rod-like form. A standard General Electric XRD unit was employed in making the patterns. Sample-to-film distance of 5 cm. and a 0.025″ pinhole collimator were used in recording patterns of the alpha forms. In obtaining patterns of the sub alpha and beta forms, 10-

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