temperature changes from 57 to −19°. This effect has also been observed by Wöhler and Wenzel.[19] This increase in adsorption by decreased temperature might also lend itself to improving separations of difficultly separable substances.

It cannot be stated whether the effects observed here are due to solubility *per se* or to some property which varies with solubility. It is likely that the phenomenon of increased adsorption of fatty acids with depressed solubility is the same phenomenon of increased adsorption of acids by addition of salts to the solvent as described by Wiegener, *et al.*,[18] and referred to by Tiselius as "salting out adsorption."[20] It may also be that the effect is related to surface tension phenomena as suggested by Wiegener, *et al.* The effects of changing solvents in chromatography to alter adsorption of various substances is common knowledge, and it may be that the results reported here are but an extension of that principle.

The spreading of isotherms by altering the character of the solvent should be useful in separating hitherto difficultly separable substances. In the other direction, this principle can be extended to include members of this homologous series only slightly soluble in alcohol. In this latter case the solubility can be increased by mixing alcohol with a solvent in which the solute is more highly soluble. For example, separation of behenic acid from palmitic and stearic acids has been accomplished by using chloroform–alcohol in which behenic acid is sufficiently soluble.

It appears from these experiments that a higher homolog is the displacer of choice. The most suitable displacer seems to be that member of the homologous series which is next lower in solubility to the substances to be displaced. By using that displacer in a solvent mixture which just dissolves the desired concentration of the displacer, one automatically chooses suitable conditions of solubility for the sample.

Summary

1. Adsorption isotherms for lauric and myristic acids in 95% alcohol on a series of varied adsorbents are given.
2. The depression of solubility of fatty acids in alcohol by admixture with water, or by lowering temperature increases adsorption and spreads isotherms. The lowered solubility caused by addition of water increases separability of fatty acids as shown in frontal and displacement analysis. The use of isotherms to predict the character of displacement diagrams for fatty acids has been verified.
3. The best displacer found thus far for a fatty acid is its nearest homolog of lower solubility in a solvent which just dissolves the desired concentration of displacer.

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(19) Wöhler and Wenzel, *Kolloid Z.*, **53**, 273 (1930).

(20) Tiselius, *Arkiv för Kemi. Mineral. Geol.*, **26B**, 1 (1948).

[CONTRIBUTION FROM THE S. A. M. LABORATORIES OF THE MANHATTAN PROJECT]

The Rearrangement of Chlorofluorocarbons by Aluminum Chloride[1]

BY WILLIAM T. MILLER, JR.,[2] EDWARD W. FAGER[3] AND PAUL H. GRISWALD[4]

The reaction of aluminum chloride with chlorofluoromethanes and ethanes to replace fluorine by chlorine has been reported by Henne,[5,6] who found in attempting Friedel–Crafts reactions that only fluorine-free condensed products were formed. Similarly, benzotrifluoride yielded only benzotrichloride by reaction with aluminum chloride, but from 1,1,2-trichlorotrifluoroethane the intermediate chlorine replacement product tetrachloro-1,1-difluoroethane was isolated in small amounts. This last reaction was developed by Miller as a synthetic procedure[7] and is of general interest as illustrating a method for the preparation of chlorofluoro compounds with structures not directly obtainable by the progressive replacement of chlorine by fluorine.[8] Relatively mild reaction conditions were found to be necessary in order to avoid the complete replacement of fluorine by chlorine observed by Henne and his associates.

In the present work which was originally undertaken to extend the fluorine replacement reaction to other chlorofluorocarbons, the synthesis of tetrachloro-1,1-difluoroethane from 1,1,2-trichlorotrifluoroethane was re-examined and more efficient conditions for the preparation of this material developed. In addition, it was found that the reaction involved not only replacement of fluorine by chlorine but rearrangement as well. The recovered low-boiling fraction which boiled at the same point as the starting material, 1,1,2-trichlorotrifluoroethane was found to be largely 1,1,1-trichlorotrifluoroethane. Under the conditions described below the reaction proceeded as shown

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[1] This paper was largely based on work done for the Manhattan Project under Contract No. W-7405-Eng-50 at S. A. M. Laboratories, Columbia University and under contract No. W-7405-Eng-26, Supplement No. 4 at S. A. M. Laboratories Carbide and Carbon Chemicals Corporation, New York City.

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[5] Henne and Leicester, THIS JOURNAL, **60**, 864 (1938).

[6] Henne and Newman, *ibid.*, **60**, 1697 (1938).

[7] Miller, *ibid.*, **62**, 993 (1940).

[8] Locke, Brode and Henne, *ibid.*, **56**, 1726 (1934).

$$CCl_2FCClF_2 \xrightarrow{AlCl_3} CCl_3CF_3,\ 50\% + CCl_3CClF_2,\ 40\% \\ + CCl_3CCl_2\ 5\% + \text{recov. } CCl_2FCClF_2\ 5\%$$

When the low-boiling fraction from one run was retreated with aluminum chloride the rearranged product was obtained pure.

When 1,2,3-trichloropentafluoropropane, $CClF_2CClFCClF_2$, which while not entirely homogeneous was at least 90% pure, was treated with aluminum chloride, the principal products were $CClF_2CCl_2CF_3$ and $CCl_3CCl_2CF_3$. These substances constituted 90% of the recoverable material. Their formation further indicated the tendency to form trifluoromethyl groupings by rearrangement of saturated chlorofluorocarbons. Similarly, tetrachloro-1,2-difluoroethane could be converted into tetrachloro-1,1-difluoroethane, but in poor yield due to the greater tendency for replacement of fluorine by chlorine to occur.

The stability of chlorofluoro groupings toward reaction with aluminum chloride to replace fluorine paralleled their stability toward chlorine replacement by reagents such as antimony trifluoride, that was: $(CF_3-) > CClF_2- > CCl_2F- > (CCl_3-)$. No evidence was obtained for the presence of CCl_3CCl_2F, CCl_2FCCl_2F or of $CCl_2FCCl_2CF_3$ in the reaction mixtures studied and the trifluoromethyl groupings once formed in the aliphatic chlorofluorocarbons resisted further attack by aluminum chloride in contrast to benzotrifluoride.[2]

The rearrangement reaction was shown to proceed by an intramolecular mechanism and, as far as we are aware, represents the first intramolecular rearrangement involving shift of fluorine which has been demonstrated. However, since this paper was first prepared, Henne and Newby[9] and Whaley and Davis[10] have reported rearranged products obtained in fluorinating allylic chlorine compounds with antimony salts. Data establishing whether or not processes of this type may involve intramolecular rearrangement of fluorine or whether rearrangement can be carried out without replacement are not yet available. Whaley and Davis concluded from their work that, "at no time was there any evidence for the migration of a fluorine atom."

The driving force for the rearrangement reaction appears to be due to the formation of more stable halogen clusters[11] and it is of interest to note that intermolecular disproportionation reactions promoted by aluminum chloride and leading to the formation of more highly fluorinated, and chlorinated, compounds have been observed with chlorofluoromethanes as well as replacement of fluorine by chlorine.[12] The remarkable chemical stability of the CF_3- grouping is well known. The usual difficulty of its formation by substitution of chlorine in saturated systems is due to an unusually high energy barrier for the last step, and the clean-cut orientation frequently observed for the progressive substitution of chlorine by fluorine[13] is clearly a rate phenomenon.[14]

The rearrangement reaction was indicated as an intramolecular process since it did not involve chlorine exchange with the catalyst. This was shown by treating CCl_2FCClF_2 for a short time with aluminum chloride containing radioactive chlorine followed by fractionation of the products, decomposition of the fractions corresponding to $C_2Cl_3F_3$ and $C_2Cl_4F_2$ by sodium peroxide fusion, and precipitation of the chlorine from the fusion mixtures as silver chloride for counting. Radioactivity was found in the fraction corresponding to $C_2Cl_4F_2$ formed by replacement but was absent in the fraction corresponding to $C_2Cl_3F_3$ which was shown to contain 20–30% of CCl_3CF_3 formed by rearrangement. This result suggested a mechanism of rearrangement in which the initial step involved coördination of the fluorine atom to be transposed with aluminum chloride. Rearrangement without chlorine interchange or replacement with chlorine from the aluminum chloride might then occur. On the other hand, rearrangement initiated by coördination with chlorine would be expected to result in chlorine interchange.

The rearrangement reaction provides a new-type synthetic process for the preparation of chlorofluorocarbons which in suitable cases avoids the usual difficulty experienced in obtaining trifluoromethyl groupings by chlorine replacement, and permits the preparation of specific compounds not otherwise readily obtainable.

Experimental

1,1,2-Trichlorotrifluoroethane.—Conditions favorable to the formation of the rearrangement and replacement products were as follows. One mole of powdered anhydrous aluminum chloride was added to six moles of CCl_2FCClF_2 and the mixture heated to reflux with stirring in an oil-bath maintained at 55–60° for five hours. Stirring was accomplished with a Hershberg type stirrer and maintained the aluminum chloride in suspension. The reaction mixture was poured into cracked ice, the organic layer separated, washed with water and dried by passage through a short column packed with phosphorus pentoxide on glass wool. Distillation through an eleven-plate column gave two fractions boiling at 46–48° and 91–92° and a small residue.

The low-boiling fraction consisted of 90% CCl_3CF_3 and 10% CCl_2FCClF_2 as determined by melting point. It constituted 50–55% of the original weight of material. Retreatment of this material with aluminum chloride under similar conditions gave an almost quantitative yield of CCl_3CF_3 which had the following properties: m. p. 13.5–14.0°; b. p. 46.4°; $n^{20}D$ 1.3603; d^4_{20} 1.5771; reported for CF_3CCl_3[15]: m. p. 14.2°; b. p. 45.9°; $n^{20}D$ 1.3610; d^4_{20} 1.579. Calcd. for $C_2Cl_3F_3$: mol. wt., 187.5. Found: mol. wt., 187.

The higher-boiling fraction which corresponded to approximately 40% of the original weight of material con-

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[9] Henne and Newby, THIS JOURNAL, **70**, 130 (1948).

[10] Whaley and Davis, *ibid.*, **70**, 1026 (1948).

[11] See also ref. 10.

[12] U. S. Patents 1,994,035, 2,426,637, 2,426,638.

[13] Henne and Midgley, THIS JOURNAL, **58**, 883 (1936).

[14] The purity of chlorofluoro compounds prepared in the presence of metal halides and under conditions not definitely shown to avoid rearrangment, in general, requires careful demonstration.

[15] Henne, *ibid.*, **62**, 2051 (1940).

sisted of CCl_3CClF_2 which had the following properties: m. p. 40.5–40.6°; b. p. 91–92°; reported for CCl_3-$CClF_2$[12]: m. p. 40.6°; b. p. 91°. The still residue corresponded to 5% of the original material and was shown to be largely hexachloroethane. Longer reaction times resulted in the formation of larger quantities of this material.

1,2,3-Trichloropentafluoropropane.—The conditions used exactly paralleled those reported above except that a bath temperature of 80–90° was necessary to maintain reflux. For unexplained reasons the recovery was never more than 60% of the starting material.[16] Distillation through an eleven-plate column gave two principal fractions boiling at 70–72° and at 151–152°.

The low-boiling fraction which constituted 70% of the recovered material after redistillation had the following properties: m. p. −5°; b. p. 71–72°; $n^{25}\mathrm{D}$ 1.3490. An authentic sample of $CClF_2CCl_2CF_3$[17] had the following properties: m. p. −4.3°; $n^{25}\mathrm{D}$ 1.3490. A mixture of the two samples melted −4 to −5°.

The high b. p. material which composed 20% of the recovered material had the following properties after redistillation and crystallization from alcohol: m. p. 108.9–109.2°, b. p. 151.8–152.0°; reported for $CCl_3CCl_2CF_3$ m. p. 109.0°, b. p. 153.1°. No other $C_3Cl_5F_3$ compound melts near $CCl_3CCl_2CF_3$.[17]

Acknowledgment.—We are indebted to Dr. J. R. Dunning and members of the Columbia University cyclotron group for the preparation of radioactive chlorine and to Drs. J. Bigeleisen and A. Kirschenbaum for counting analytical samples.

Summary

Aluminum chloride has been found to cause rearrangement as well as replacement of fluorine by chlorine, when reacting with some saturated chlorofluorocarbons. The rearrangement reaction was shown to proceed by an intramolecular mechanism and to lead to the formation of compounds containing two or three fluorines on one carbon.

ITHACA, NEW YORK RECEIVED[18] AUGUST 4, 1949

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[16] The possible formation of volatile cleavage products corresponding to a reversed Prins type reaction was not investigated.

[17] Henne and Whaley, THIS JOURNAL, **64**, 1157 (1942).

[18] This paper was originally submitted February 4, 1949.

[CONTRIBUTION FROM THE DEPARTAMENTO DE QUÍMICA DA FACULDADE DE FILOSOFIA, CIÊNCIAS E LETRAS DA UNIVERSIDADE DE SÃO PAULO, BRASIL]

The Action of Raney Nickel upon Sulfur Compounds. II. Mercaptals, Mercaptols and Disulfides[1,2]

BY H. HAUPTMANN AND B. WLADISLAW

Recently we reported briefly upon two different types of reactions observed when Raney nickel is allowed to act upon aromatic mercaptals and mercaptols. During these experiments the Raney nickel had to be freed from the hydrogen adsorbed in the course of its preparation by heating *in vacuo* and the reaction had to be carried out in the absence of hydrogen donating solvents. When aromatic mercaptals and mercaptols were refluxed in xylene solution in the presence of Raney nickel previously heated at 100°, binuclear hydrocarbons were formed. Thus, from formaldehyde diphenylmercaptal (I) we were able to isolate diphenyl in a yield of 9%. This transformation is analogous to the conversion of diphenyl sulfide into diphenyl[1]. It has been discussed[3] as a possible side reaction in hydrogenolytic desulfurization and called a "Wurtz type reaction," but previously it had not been observed by any investigator.

From mercaptals of benzaldehyde (II, III) or mercaptols of acetophenone (IV), stilbene or its substitution products were obtained in yields up to 37%. The formation of stilbene under these conditions is not entirely unexpected in view of the report by Campaigne, *et al.*,[4] who isolated *trans*-dimethylstilbene (18% yield) after treating trithioacetophenone with Raney nickel in xylene solution and those of Bergmann, *et al.*,[5] who obtained 1,2-di-(9-phenanthryl)-ethylene from polymeric phenanthryl-9-thioaldehyde.[6]

Campaigne, *et al.*, supposed that their low yield was due to hydrogenolytic formation of volatile ethylbenzene, and this is quite probable since they made no attempt to remove the adsorbed hydrogen from the Raney nickel. We, too, considered hydrogenolytic desulfurization to benzene and toluene to be the cause of our relatively low yields of diphenyl and stilbene. Therefore, we heated the Raney nickel *in vacuo* at 200° which resulted in the evolution of a considerable amount of hydrogen. In the following, this will be recognized as "hydrogen-free Raney nickel" in contrast to the "hydrogen-poor Raney nickel" previously heated at only 100°. With hydrogen-free Raney nickel the yield of stilbene was im-

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[1] Paper I of this series, H. Hauptmann, B. Wladislaw and P. F. Camargo, *Experientia*, **4**, 385 (1948).

[2] This paper is extracted from a thesis presented to the Faculdade de Filosofia, Ciências e Letras da Universidade de São Paulo by B. Wladislaw in partial fulfillment of the requirements for the degree of "Dr. em Ciencias."

[3] R. Mozingo, D. E. Wolf, S. A. Harris and K. Folkers, THIS JOURNAL, **65**, 1013 (1943).

[4] J. K. Cline, E. Campaigne and J. W. Spies, *ibid.*, **66**, 1136 (1944).

[5] F. Bergmann and S. Israelashwili, *ibid.*, **67**, 1951 (1945).

[6] Stilbenes are the main reaction products when polymeric thioaldehydes or thioketones are heated with copper bronze. See J. H. Wood, J. A. Bacon, A. W. Meibohm, W. H. Throckmorton and G. P. Turner, *ibid.*, **63**, 1334 (1941); R. C. Fuson and C. E. Best, *ibid.*, **67**, 155 (1945); L. Gattermann, *Ber.*, **28**, 2869 (1895), and **29**, 2944 (1896). Detailed bibliographic survey by E. Campaigne, *Chem. Revs.*, **39**, 1 (1946).