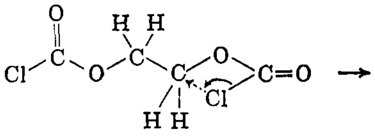
substitution and elimination. There were possibly three major primary products: vinyl chloroformate, 2-chloroethyl chloroformate, and 1,2-dichloroethane. The elimination reaction became important only at higher temperatures (above 460°). These results agree with Lewis and Herndon's findings on other chloroformates.

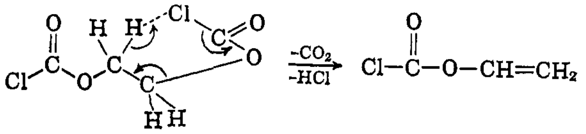
According to Lewis and Herndon, the substitution reaction of chloroformates is presumably a one-step reaction through a cyclic transition state of ROCOCl to RCl. The mechanism was supported by a large negative entropy of activation, the relative reactivities of different alkyl chloroformates, retention of configuration, and absence of rearranged alkyl chlorides.



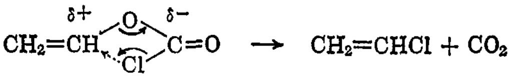
$$CO_2 + ClOCOCH_2CH_2Cl \longrightarrow ClCH_2CH_2Cl$$

The decomposition results (Table I) show that with a high feed rate 2-chloroethyl chloroformate was present in an amount (weight) at least twice that of 1,2-dichloroethane. As the feed rate decreased, the amount of 1,2-dichloroethane increased.

The elimination reaction[2] for other chloroformates was shown by Lewis and Herndon to proceed *via* a more polar transition state. In the case of ethylene glycol bis(chloroformate), the six-membered cyclic transition state may be shown as follows.



Vinyl chloride may be formed *via* the transition state given below. This substitution is one of the best



examples for an S_Ni mechanism, because the existence of the ion-pair intermediate is highly questionable as a result of the unfavorable structure of a vinyl cation.

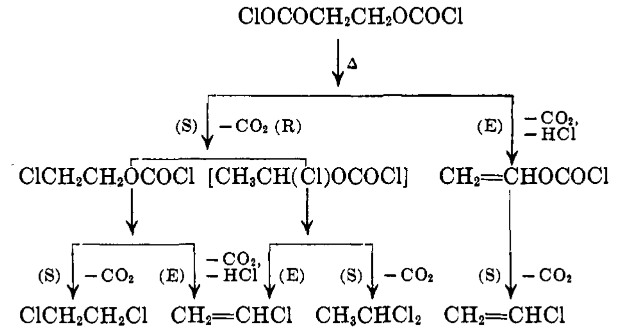
One of the products obtained with a slow feed rate was 1,1-dichloroethane. We assume that the logical source of this compound was 1-chloroethyl chloroformate as reported by Küng. The possible involvement of 1-chloroethyl chloroformate needs further investigation.

Conclusion

The preceding discussion on mechanism and the experimental results suggest that the yield of vinyl chloroformate can be increased by the following three methods: (1) by raising the temperature slightly above 460° (It should be noted that the minimum temperatures were found to be different in different apparatus.); (2) by using a high feed rate (With a high feed rate, the formation of 1-chloroethyl chloroformate and 1,1-dichloroethane could be prevented. Also, with a high feed rate, the further decomposition of vinyl chloroformate into vinyl chloride could be minimized.); and (3) by using a diluent such as nitrogen (The use of a diluent could minimize the formation of secondary products, perhaps simply because of better heat transfer.).

The relationship between the primary and the secondary decomposition products may be summarized by Scheme I.

Scheme I



S = substitution, E = elimination, R = rearrangement

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Reduction of Polyfluoroalkyl Nitriles with Sodium Borohydride

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During a study of the effects of various highly fluorinated molecules on the properties of cotton textiles, it was necessary to prepare certain representative primary polyfluoroalkylamines.

A compilation[2] of methods for preparing primary fluorinated alkylamines reveals that the reduction of the corresponding carboxamides with lithium aluminum hydride[3a,b] is of general utility. Side reactions[3b] leading to aldehyde formation lower the yields somewhat and certain precautions which appear necessary in this procedure[3b] because of the reactive nature of the hydride or because of the nature of the reaction intermediates[4a,b] may prove troublesome. A recent report[5] which appeared near the completion of our work indicates that high yields of 1,1-dihydroperfluoro-

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[1] One of the laboratories of the Southern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.

[2] A. M. Lovelace, D. A. Rausch, and W. Postelnek, "Aliphatic Fluorine Compounds," Reinhold Publishing Corp., New York, N. Y., 1958, pp. 285–288.

[3] (a) J. E. Carnahan and H. J. Sampson, U. S. Patent 2,646,449 (1953); (b) D. R. Husted and A. H. Ahlbrecht, U. S. Patent 2,691,043 (1954).

[4] (a) T. S. Reid and G. H. Smith, *Chem. Eng. News*, **29**, 3042 (1951); (b) W. Karo, *ibid.*, **33**, 1368 (1955).

[5] M. Sander, *Monatsh. Chem.*, **95**, 608 (1964).

alkylamines may be obtained by lithium aluminum hydride reduction of perfluoronitriles. This latter method overcomes the complications caused by carbonyl-containing by-products.

In view of the possibly troublesome nature of routes to these amines utilizing lithium aluminum hydride it was deemed desirable to investigate methods using less reactive complex metal hydrides. Because of the ease of handling sodium borohydride, it was the reagent of choice.

A search of the literature revealed that amine formation from the sodium borohydride reduction of neither nitriles nor primary amides containing polyfluoroalkyl groups has been reported.[6,8a,b,10]

Addition of three representative polyfluoroalkyl nitriles to a stirred slurry of sodium borohydride in the dimethyl ether of diethylene glycol (diglyme) gave moderate to high yields of the corresponding amines after the reaction mixture was treated with aqueous acid or, preferably, sodium hydroxide. Apparently the amine is formed *via* some type of boron-containing complex since gas chromatographic examination of the mixture of sodium borohydride and perfluorocaprylonitrile in diglyme immediately after refluxing but prior to alkaline hydrolysis revealed, in addition to diglyme and minute amounts of free amine and unchanged nitrile, a large amount of an unknown material which is assumed to be the intermediate complex. Subsequent steam distillation of the alkaline reaction mixture gave the free amine which could be isolated either by ether extraction or by conversion to the hydrochloride salt.

At least 2 moles of sodium borohydride/mole of nitrile were employed to ensure complete reduction of the nitriles. The reductions were carried out for 1–1.5 hr. at the reflux temperature of diglyme in the case of the higher boiling nitriles, while perfluorobutyronitrile was reduced at room temperature.

Since nitriles are normally not reduced by sodium borohydride,[8b,10] it is assumed that strong electron withdrawal by a polyfluoroalkyl group is sufficient to render the nitrile function amenable to attack by the hydride.

Experimental Section[11]

1,1-Dihydroperfluorobutylamine.—An intimate mixture of 25.0 g. (0.117 mole) of perfluorobutyramide and 50 g. (0.35 mole) of phosphorus pentoxide in a flask surmounted by a Dry Ice–acetone cooled condenser was heated for about 1.5 hr. at 140–170° and the nitrile formed was slowly transferred by means of a nitrogen stream into two traps cooled by Dry Ice–acetone. The nitrile was then led during about 1.5 hr. into a three-necked flask surmounted by a Dry Ice–acetone cooled condenser. The reaction flask contained a magnetically stirred slurry of 8.85 g. (0.234 mole) of sodium borohydride in 140 ml. of dry diglyme at about 25°. The addition was slow enough to maintain the reaction temperature at about 32°. After the addition, about 150 ml. of ice–water and 10 ml. of 50% sodium hydroxide were cautiously added before steam distilling the mixture. About 450 ml. of distillate was collected and extracted with ether, and the extract was saturated with hydrogen chloride. The 1,1-dihydroperfluorobutylamine hydrochloride weighed 12.33 g. after washing with ether: m.p. 310–314° dec. (sealed capillary); its neutralization equivalent was 235 (calcd. 234.5). Recrystallization from an absolute ethanol–ether mixture gave an analytical sample, m.p. 317–319° dec. (sealed capillary preheated to 300°).

Anal.[12] Calcd. for $C_4H_5ClF_7N$: 20.40; H, 2.14; N, 5.95. Found: C, 20.23; H, 2.11; N, 5.99.

About 0.6 g. of unchanged amide was recovered from the phosphorus pentoxide by an ether wash, giving a 46.1% yield of amine salt based on amide utilized. Treatment of the salt with sodium hydroxide gave the pure amine, b.p. 69°,[3b] upon distillation from barium oxide.

Anal.[12] Calcd. for $C_4H_4F_7N$: C, 24.13; H, 2.02; F, 66.81; N, 7.04. Found: C, 24.45; H, 2.26; F, 66.64; N, 7.10.

Its acetyl derivative melted at 50.5–52°.[13]

1,1,9-Trihydroperfluorononylamine.—Ethyl 9-hydroperfluoropelargonate, b.p. 112° at 40 mm., $n^{25}\mathrm{D}$ 1.3203, $C{=}O$ at 5.64 μ ($CHCl_3$), was formed in 46% yield by esterification of the acid with concentrated sulfuric acid as catalyst.

Anal. Calcd. for $C_{11}H_6F_{16}O_2$: C, 27.86; H, 1.28; F, 64.11. Found: C, 26.25; H, 1.29; F, 63.02.

Treatment of the ester with gaseous ammonia gave the amide, m.p. 136–138°,[3a] which was then dehydrated with phosphorus pentoxide to give an 86% yield of 9-hydroperfluoropelargononitrile, b.p. 144°, $C{\equiv}N$ at 4.44 μ ($CHCl_3$).

Anal. Calcd. for $C_9HF_{16}N$: C, 25.31; H, 0.24; F, 71.18; N, 3.28. Found: C, 24.38; H, 0.15; F, 72.84; N, 3.23.

Reaction of the nitrile with excess sodium borohydride for 1.5 hr. at the reflux temperature of diglyme gave a 61.8% yield of 1,1,9-trihydroperfluorononylamine hydrochloride, m.p. 264–266° dec. (sealed capillary), neut. equiv. 476 (calcd. 467.5). The free amine distilled at 84–90° at 12–14 mm.[3a]

1,1-Dihydroperfluorooctylamine.—Reduction of perfluorocaprylonitrile with excess sodium borohydride for 1 hr. at the reflux temperature of diglyme gave a 73% yield of 1,1-dihydroperfluorooctylamine, b.p. 75–75.5° (50 mm.),[3b] $n^{27}\mathrm{D}$ 1.3051.

Anal.[12] Calcd. for $C_8H_4F_{15}N$: C, 24.07; H, 1.01; F, 71.41; N, 3.51. Found: C, 24.11; H, 1.08; F, 71.34; N, 3.80.

The hydrochloride salt decomposed in a sealed capillary at 278–280°.

Anal.[12] Calcd. for $C_8H_5ClF_{15}N$: C, 22.06; H, 1.16; F, 65.43. Found: C, 21.70; H, 1.65; F, 65.62.

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[6] In a patent specification[3a] it is stated that sodium borohydride is effective in reducing polyfluoroalkylcarboxamides to amines but no supporting experimental data are given. In our hands reaction of $CF_3(CF_2)_6CONH_2$ with excess sodium borohydride in the dimethyl ether of diethylene glycol (diglyme) either at room temperature or at reflux gave $CF_3(CF_2)_6CH_2OH$ and only traces of the amine.[7]

[7] S. E. Ellzey, Jr., and J. S. Wittman, III, unpublished data.

[8] (a) H. P. Johnston [U. S. Patent 3,026,355 (1962)] reported that acetamide and benzamide were reduced to the corresponding amines by *deficient* amounts of sodium borohydride in a solvent-free system. (b) In our hands, a variety of nonfluorinated primary amides gave mainly the corresponding *nitriles* upon treatment with *excess* sodium borohydride in refluxing diglyme.[9]

[9] S. E. Ellzey, Jr., Charles H. Mack, and W. J. Connick, Jr., unpublished results.

[10] N. G. Gaylord, "Reduction with Complex Metal Hydrides," Interscience Publishers, Inc., New York, N. Y., 1956, p. 750.

[11] Melting points and boiling points are uncorrected. Analyses were performed by Midwest Microlab, Inc., Indianapolis, Ind., and Galbraith Laboratories, Inc., Knoxville, Tenn.

[12] This compound was reported without analytical data in ref. 3b.

[13] D. R. Husted and A. H. Ahlbrecht, U. S. Patent 2,743,297 (1956).

Synthesis and Base Strength of 2,4,6-Tri-*t*-butylphenylhydrazine

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We have synthesized 2,4,6-tri-*t*-butylphenylhydrazine (I) in order to determine the effects of the *t*-butyl groups on the basicity. Our work can be regarded as an extension of observations by others on the basicity of 2,4,6-tri-*t*-butylaniline[1] (II) and 2,6-di-*t*-butylpyridine[2] (III).

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[1] (a) P. D. Bartlett, M. Roha, and R. M. Stiles, *J. Am. Chem. Soc.*, **76**, 2349 (1954); (b) B. M. Wepster, *Rec. trav. chim.*, **76**, 357 (1957); (c) J. Burgers, M. A. Hoefnagel, P. E. Verkade, H. Visser, and B. M. Wepster, *ibid.*, **77**, 491 (1958).

[2] H. C. Brown and B. Kanner, *J. Am. Chem. Soc.*, **75**, 3865 (1953).