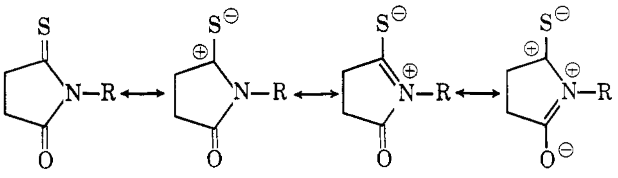
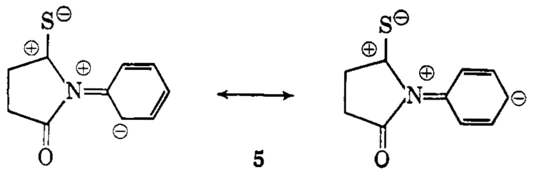
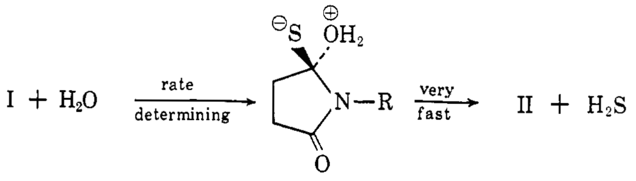
bility of octet expansion in sulfur[18a,19] and probably represents a major reason for the rapid hydrolysis to imide. In thionimides four resonance structures, **1**, **2**, **3**, and **4** contribute to the electronic character of the C=S group. Excluding steric effects introduced by R, the greater the contribution of resonance structure **3**, the slower should be nucleophilic attack by water since the effective positive character on carbon of the C=S group is decreased.[20] The fact that thionimides contain an additional C=O in conjugation with the electron pair on nitrogen (**4**) accounts for the greater instability of C=S in thionimides than in the related thionamides where the polarized form **2** (or **4**) would not exhibit as great an influence on the transition state with respect to the ground state of the molecule. Introduction of phenyl on the imide nitrogen provides another contributing structure **5**, the influence of which is to increase the net positive character at the reaction center. Placement of electron-withdrawing substituents in the *para* position increases the contribution made by resonance form **5** and the rate of hydrolysis is accelerated. A possible rationalization is dependent upon a rate-determining step involving formation of the *solvated*, tetrahedral intermediate III which rapidly collapses to imide II.



1 2 3 4



5



III

More detailed explanations concerning the minor deviations of the observed rates from the rate calculated using $\rho = +0.348$ and the σ constant for p-CH_3O and p-halogen derivatives must await more extensive studies involving temperature and pH profiles.[17] However, it does appear that the rates of hydrolysis parallel the electronegativity constant[21] for the p-halogen. This may indicate that polar effects are more important in these systems than would be reflected by the σ constant since +R contributions of *para* substituents are partially blocked by insertion of N between the aromatic ring and the reaction center.

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[19] R. B. Woodward and R. H. Eastman, *J. Am. Chem. Soc.*, **68**, 2229 (1946); R. Rothstein, *J. Chem. Soc.*, 1558 (1940).

[20] Alternatively, the greater the resonance contribution by **2** (or **4**) the smaller should be the difference in energy between transition and ground states. This decrease in energy of activation would be reflected in an accelerated rate of hydrolysis.

[21] L. C. Pauling, "The Nature of the Chemical Bond," 2nd Ed., Cornell University Press, Ithaca, N. Y., 1940, pp. 58, 59; E. S. Gould, "Mechanism and Structure in Organic Chemistry," Holt, Rinehart and Winston, New York, N. Y., 1959, pp. 39–41; H. O. Pritchard and H. A. Skinner, *Chem. Rev.*, **55**, 745 (1955).

Reactions of Perfluoroalkyl Nitriles. V. Synthesis of Perfluoroacyl Imidates[1]

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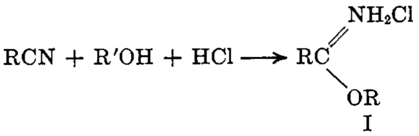
Received February 5, 1965

Stable alkyl perfluoroacyl imidates, $R_FC(=NH)OR$, were prepared by the base-catalyzed addition of methyl, isopropyl, and 2,2,2-trifluoroethyl alcohols to perfluoroalkyl nitriles. Tertiary alcohols did not produce imidates under the same conditions, apparently owing to steric hindrance and the tendency of the perfluoroalkyl nitriles toward trimerization. Phenol formed phenyl perfluoroacyl imidate. In a similar reaction the >N–OH group of propanone oxime added to perfluoroalkyl nitriles to produce O-(perfluoroalkylimidoyl)propanone oxime $R_FC(=NH)ON=C(CH_3)_2$.

The classical synthesis of imidates by Pinner[2] involved the condensation of a nitrile and an alcohol under anhydrous conditions in the presence of hydrogen chloride, and the imidate hydrochloride I was the product obtained. The free imidates were obtained by treating the hydrochlorides with a base.



$$RCN + R'OH + HCl \longrightarrow RC\begin{matrix}\diagup NH_2Cl \\ \diagdown OR\end{matrix}$$

I

Steinkopf and Malinowski[3] studied the effect of negative substituents on nitriles and found that although many α- and β-halogen-substituted nitriles behaved normally in the Pinner synthesis, trichloroacetonitrile, nitroacetonitrile, dichloroacetonitrile, tribromoacetonitrile, and dichloronitroacetonitrile gave amides and no imidates. Dibromoacetonitrile gave both the amide and the imidate. These results were obtained using aliphatic alcohols. Houben[4] found that the Pinner synthesis was successful if aromatic

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[1] (a) This investigation was supported by Public Health Service Research Grant CA-05083 from the National Cancer Institute. (b) For previous paper in this series, see H. C. Brown and P. D. Schuman, *J. Org. Chem.*, **28**, 1122 (1963).

[2] A. Pinner and F. Klein, *Ber.*, **10**, 1889 (1877).

[3] W. Steinkopf and W. Malinowski, *ibid.*, **44**, 2898 (1911).

[4] J. Houben, *ibid.*, **59**, 2878 (1926).

alcohols were used with nitriles containing more than one negative substituent.

The usefulness of the Pinner synthesis is limited by the occurrence of the so-called "Pinner cleavage," by which the imidate hydrochloride decomposes into the corresponding amide and alkyl chloride. McElvain and Nelson[5] have shown that negative substituents on the nitrile have a destabilizing effect on the corresponding imidate hydrochlorides.

Another approach to the synthesis of imidates was provided by Marshall and Acree[6] who studied the base-catalyzed formation of imidates; they found that imidate formation was promoted by the presence of electron-attracting groups on the nitrile. Schaeffer and Peters[7] extended these studies of base-catalyzed formation of imidates and Cramer[8] and co-workers were successful in synthesizing a wide variety of alkyl and aryl trichloroacetimidates.

It is apparent that those nitriles which are unsuited for base-catalyzed reactions usually give excellent results in the Pinner method of synthesis, and conversely, the nitriles which are most reactive in the base-catalyzed synthesis often give unstable imidate hydrochlorides.

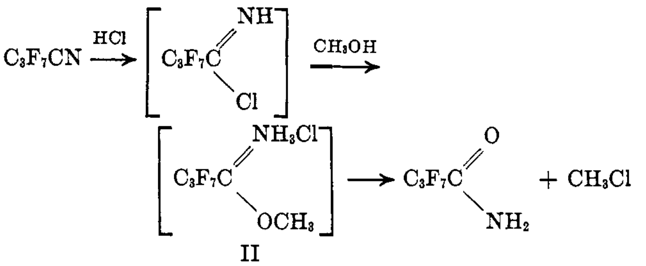
The reaction of perfluoroalkyl nitriles with alcohols has not previously been studied extensively and the information available in the literature is rather confusing. Brown and Pater[9] reported the base-catalyzed synthesis of the perfluoroalkylthioimidates from the reaction of perfluoroalkyl nitriles with mercaptans but stated that under similar conditions alkyl perfluoroacyl imidates apparently did not form. Johnson and Woodburn[10] reported a marked solvent effect when using methanol in the reaction of perfluoroacetonitrile with several alkyldiamines but thought the intermediate formation of an imidate unlikely since a strongly basic catalyst was not present.

The present work shows that perfluoroacyl imidates may be prepared easily with basic catalysts in excellent yields. Perfluoroacetonitrile and perfluorobutyronitrile reacted rapidly and exothermally with methyl alcohol and with 2,2,2-trifluoroethylalcohol containing low concentrations of basic catalysts. No reaction was observed in the absence of a catalyst, even at elevated temperatures. Sodium alcoholates and tertiary amines were equally effective catalysts for reaction with primary alcohols.

The alkyl perfluoroacyl imidates were easily purified; for example, pure ethyl perfluoroacetimidate was distilled directly from the reaction mixture. Methyl perfluorobutyrimidate formed a constant-boiling mixture with methyl alcohol, and washing with water was necessary to separate the insoluble imidate. Trifluoroethyl alcohol, although considered to be at least 10^4 times more acidic than ethyl alcohol, and to approach the acidity of phenol, added readily to the perfluoroalkyl nitriles under the same conditions as those used for methyl alcohol.

Dimethyl perfluoroglutarimidate formed readily under similar conditions; however, this compound lost methyl alcohol on heating to give a polymeric material. This reaction is probably similar to the loss of ammonia that occurs on heating perfluoroglutarimidine,[11] and which gives polymers whose structure is a network of triazine rings connected by perfluoroalkyl chains.

The formation of alkyl perfluoroacyl imidates using an acidic catalyst was investigated briefly. Hydrogen chloride readily catalyzed the addition of methyl alcohol to perfluorobutyronitrile but the resulting perfluoroacyl imidate hydrochloride was unstable and underwent decomposition to perfluorobutyramide and methyl chloride. The identification of these two final products provided strong evidence for the formation of the intermediate imidate hydrochloride II.



II

The ability of hydrogen chloride to catalyze addition to perfluoroalkyl nitriles was shown more clearly in the formation of methyl perfluoroacetothioimidate hydrochloride. The replacement of oxygen by sulfur greatly enhances the stability of this imidate hydrochloride, which was first prepared by Brown and Pater[9] from the free base. It was found that this hydrochloride could be prepared directly from perfluoroacetonitrile in the classical Pinner method in a 74% yield.

The *n*-alkyl perfluoroacyl imidates were colorless liquids with pleasant odors resembling the characteristic odor of esters. They were stable at room temperature for extended periods without decomposition. Physical properties of the *n*-alkyl perfluoroacyl imidates are shown in Table I.

TABLE I

ALKYL PERFLUOROACYL IMIDATES

Compound	% yield	B.p., °C.	d^{26}	n^{25}
$CF_3C(=NH)OCH_3$	90	38.5–39.0	1.345	1.3203
$C_3F_7C(=NH)OCH_3$	87	75.0–76.0	1.430	1.3065
$CF_3C(=NH)OCH_2CF_3$	90	58.0–59.0	1.408	1.3035
$C_3F_7C(=NH)OCH_2CF_3$	85	93.0–93.5	1.534	1.2933
$CF_3C(=NH)OCH(CH_3)CH_3$	89	65.5–67.0	1.356	1.3225
$C_3F_7C(=NH)OCH(CH_3)CH_3$	87	101.0–101.5	1.356	1.3225
$C_3F_7C(=NH)OCH(CH_3)CF_3$[a]	..	81–82	...	...

[a] As a constant-boiling mixture with $CF_3CHOHCH_3$.

As is characteristic of most imidates, the *n*-alkyl perfluoroacyl imidates were hydrolyzed rapidly by aqueous acids to give the corresponding esters; however, *impure* imidate containing traces of basic catalysts hydrolyzed in a different manner. The stable, solid, white hydrolysis product of methyl perfluorobutyrimidate was identified by comparison with an authentic sample and found to be the perfluorobutyric acid salt of perfluorobutyramidine (III). This behavior is similar to that observed by Rule.[12]

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[5] S. M. McElvain and J. W. Nelson, *J. Am. Chem. Soc.*, **64**, 1825 (1942).

[6] E. K. Marshall and S. F. Acree, *Am. Chem. J.*, **49**, 127 (1913).

[7] F. C. Schaeffer and G. H. Peters, *J. Org. Chem.*, **26**, 412 (1961).

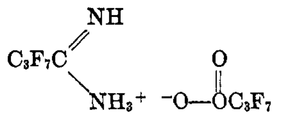
[8] F. Cramer, K. Parvelzik, and H. J. Baldauf, *Ber.*, **91**, 1049 (1958).

[9] H. C. Brown and R. Pater, *J. Org. Chem.*, **27**, 2858 (1962).

[10] R. N. Johnson and H. M. Woodburn, *ibid.*, **27**, 3958 (1962).

[11] H. C. Brown, *J. Polymer Sci.*, **44**, 9 (1960).

[12] H. G. Rule, *J. Chem. Soc.*, **113**, 3 (1918).


III

The *n*-alkyl perfluoroacyl imidates were reasonably stable to heat; methyl perfluorobutyrimidate and trifluoroethylperfluorobutyrimidate were heated in sealed ampoules at 200° for 18 hr. and recovery of the imidates was 78 and 64%, respectively.

The infrared absorption spectra of the *n*-alkyl perfluoroacyl imidates showed the characteristic N–H stretching band in the region of 2.95–3.00 μ, C–H stretching at 3.30–3.40 μ, and C=N stretching between 5.9 and 6.0 μ. Comparison of the spectra of perfluoroacyl imidates derived from dissimilar alcohols, methyl alcohol and trifluoroethyl alcohol, showed no significant shifts in the C=N band. It is interesting to note the large shift in this band caused by the replacement of the oxygen atom by a sulfur atom. Perfluoroalkylthioimidates showed C=N stretching absorption at 6.20 μ.

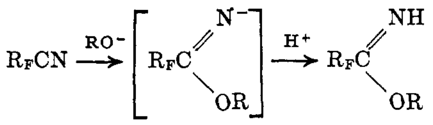
Secondary alcohols were found to be much less reactive than primary alcohols in the base-catalyzed formation of perfluoroacyl imidates. Reaction of perfluorobutyronitrile with isopropyl alcohol formed only a slight amount of isopropyl imidate under the same conditions that gave the corresponding methyl imidate in high yields. However, if the perfluoroalkyl nitriles were allowed to react with isopropyl alcohol in sealed tubes at temperatures of 60–70° for 24–48 hr. in the presence of low concentrations of anhydrous trimethylamine as a homogeneous catalyst, the corresponding isopropyl perfluoroacyl imidates were obtained in high yields. The yields and physical properties of the isopropyl perfluoroacyl imidates are shown in Table I.

The use of the strongly basic isopropylate ion as a catalyst in the reaction of isopropyl alcohol with perfluoroalkyl nitriles resulted in considerable conversion of the perfluoroalkyl nitrile to the tris(perfluoroalkyl)-1,3,5-triazines. Trimethylamine, presumably owing to its lower basicity, did not cause trimerization of the perfluoroalkyl nitrile under the reaction conditions used.

Preparation of perfluoroacyl imidates from tertiary alcohols was not successful. Trimethylamine and sodium *t*-butyl alcoholate as catalysts failed to promote the addition of *t*-butyl alcohol; in each case trimerization of the perfluoroalkyl nitrile occurred and there was no indication of even small yields of imidate.

These results are somewhat surprising since Cramer[3] has reported the preparation of trichloroacetimidates from both *t*-butyl and *t*-amyl alcohols with trichloroacetonitrile in yields of 20–30% under conditions very similar to those employed unsuccessfully using the perfluoroalkyl nitriles. However, one important difference is apparent: trimerization of the perfluoroalkyl nitriles occurred almost quantitatively, whereas Cramer does not report any side reactions of this nature using trichloroacetonitrile.

The mechanism of the formation of imidates from perfluoroalkyl nitriles using basic alcoholate catalyst probably involves the formation of the reactive intermediate IV which then acquires a proton from the alcohol to give the imidate.


IV

Two factors might be considered in accounting for the variation in formation of the perfluoroacyl imidates on going from a primary to a tertiary alcohol: first, the increasing steric hindrance due to the methyl groups attached to the α-carbon atom of the alcohol and, second, the increasing difficulty of removing a proton from increasingly α-substituted alcohols. Unfortunately these two possible hindering factors follow the same structural trend. Methyl alcohol has a measurable ionization constant of approximately 10^{-16}, isopropyl alcohol may be persuaded to part with protons only by relatively strong bases, and the deprotonation[13] of *t*-butyl alcohol requires treatment with the very strongly basic amide ion in liquid ammonia.

Certain fluorine-containing alcohols, however, furnish examples of structures increasingly branched at the α-carbon where the ease of proton loss is relatively constant. 2,2,2-Trifluoroethanol has an ionization constant of 4.0×10^{-12}, 1-methyl 2,2,2-trifluoroethanol has an ionization constant of 6.0×10^{-12}, and 1,1-dimethyl-2,2,2-trifluoroethanol has an ionization constant of 2.5×10^{-12}.[14]

Since trifluoroethyl alcohol easily formed a stable perfluoroacyl imidate, reaction of perfluorobutyronitrile with the increasingly methyl-substituted alcohols would indicate whether the controlling factor in the base-catalyzed perfluoroacyl imidate formation was steric. The ease of proton transfer would be virtually the same in each of the three alcohols. It was found that these alcohols reacted in a manner very similar to that observed in perfluoroacyl imidate formation with alcohols containing no fluorine. The secondary alcohol reacted with difficulty and the tertiary did not react at all. It thus appears that steric hindrance and the ease of trimerization of the perfluoroalkyl nitriles caused the observed trend of the reactions.

Whalley[15] found that perfluoroacetonitrile formed ketimines rather than imidates with substituted, active phenols in the presence of hydrogen chloride. In the present work it was found that phenyl perfluorobutyrimidate formed in fair yields when phenol in dioxane solution was heated with perfluorobutyronitrile at 50–60° for 24 hr. in a sealed tube containing small amounts of sodium phenolate or trimethylamine as basic catalysts. The formation of ketimines was not detected. Phenyl perfluorobutyrimidate was difficult to purify, and as expected, decomposed easily into perfluorobutyronitrile and phenol if left in contact with a basic catalyst. Pure phenyl perfluorobutyrimidate was obtained from the vacuum distillation of the crude product, prepared using sodium phenolate as a catalyst, after thorough washing with water to remove any traces of catalyst. The pure product was an unstable liquid having a sharp characteristic odor;

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[13] J. B. Conant and G. W. Wheland, *J. Am. Chem. Soc.*, **54**, 1212 (1932).

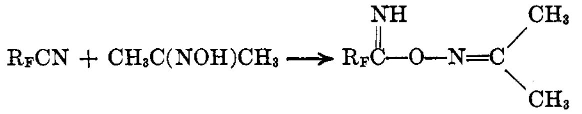
[14] A. L. Henne and R. L. Pelley, *ibid.*, **74**, 1426 (1952).

[15] W. B. Whalley, *J. Chem. Soc.*, 665 (1951).

it was found to contain substantial amounts of 2,4,6-tris(perfluoropropyl)-1,3,5-triazine after standing at room temperature for 2 months. The infrared absorption spectra of phenyl perfluorobutyrimidate showed N–H stretching at 3.0 μ, C–H stretching at 3.25 μ, and C=N stretching at 5.94 μ.

In contrast to the numerous studies investigating the addition of nitriles to the HO–C< group, there does not appear in the literature a description of the addition of nitriles to the HO–N< group. As an example of this structure for reaction with perfluoroalkyl nitriles, propanone oxime, an extremely weak base ($K_b = 6.0 \times 10^{-13}$) was chosen for its availability and the presence in the molecule of only one possible reaction site.

Perfluoroalkyl nitriles were found to add to propanone oxime very readily in diethyl ether solution in the absence of added catalyst and to produce the desired product (IV) in high yields.



$$R_FCN + CH_3C(NOH)CH_3 \longrightarrow R_FC(=NH)-O-N=C(CH_3)_2$$

IV

The O-(perfluoroacylimidoyl)propanone oximes were liquids readily purified by distillation at reduced pressure. The infrared absorption spectra of these compounds show the characteristic absorption bands of the other perfluoroalkyl imidates. N–H stretching appears at 3.0 μ, C–H stretching at 3.40 μ, and C=N stretching at 5.90 μ. An additional C=N stretching absorption band appears at 6.10 μ which is probably due to the O-substituted oxime group.

The formation of O-(perfluorobutyrimidoyl)propanone oxime was reversible; when this compound was heated above 75°, it decomposed into perfluorobutyronitrile and propanone oxime. On standing at room temperature for a prolonged period these compounds underwent rearrangements, possibly of the type found to occur with acid esters of oximes.[16]

Experimental Section

Methyl Perfluorobutyrimidate.—A solution of sodium methylate was prepared from 30 ml. of anhydrous methyl alcohol and 0.04 g. of sodium in a flask equipped with a Dry Ice–acetone cooled reflux condenser. Perfluorobutyronitrile, 45 g. (0.23 mole) was added to the solution with the temperature of the reactants maintained below 60°. The reaction mixture was then allowed to stand for 1 hr. at room temperature, washed with three 100-ml. portions of water, and dried over anhydrous calcium sulfate. The crude yield of dry product was 52.0 g. Fractionation through a packed column gave 44.5 g. (87%) of pure methyl perfluorobutyrimidate, b.p. 75–76°.

Anal. Calcd. for $C_5H_4F_7NO$: C, 26.44; H, 1.77; F, 58.56; N, 6.17. Found: C, 26.57; H, 1.93; F, 58.00; N, 6.30.

After storage of crude, moist perfluorobutyrimidate over a period of 2 months, it was found to be largely converted to a white solid which was soluble in dilute aqueous alkali and could be precipitated from basic solution on acidification. This hydrolysis product was purified by vacuum sublimation (m.p. 224°) and compared with the perfluorobutyric acid salt of perfluorobutyramidine prepared by the method of Reilly and Brown.[17] The melting point of the hydrolysis product of methyl perfluorobutyrimidate and the acid salt of the amidine were identical and the melting point of a mixture of the two showed no depression. The infrared absorption spectra of these two products were also identical.

Methyl Perfluoroacetimidate.—A solution of sodium methylate was prepared from 30 ml. of anhydrous methyl alcohol and 0.05 g. of sodium in a 100-ml. flask equipped with Dry Ice–acetone reflux condenser and magnetic stirrer. The solution was cooled by an ice bath and perfluoroacetonitrile, 30.0 g. (0.317 mole), was admitted to the flask. Since methyl perfluoroacetimidate did not form a constant-boiling mixture with methanol as did methyl perfluorobutyrimidate, the product was fractionally distilled directly from the reaction flask through a small packed column to give 36.0 g. (90%) of pure methyl perfluoroacetimidate, b.p. 38.5–39.0°.

Anal. Calcd. for $C_3H_4F_3NO$: N, 11.0. Found: N, 11.2.

2,2,2-Trifluoroethyl Perfluorobutyrimidate.—Trifluoroethanol (22.0 g., 0.22 mole) and 0.10 ml. of triethylamine were placed in a 100-ml. flask equipped with a Dry Ice–acetone cooled reflux condenser and magnetic stirrer. Perfluorobutyronitrile (39.0 g., 0.20 mole) was condensed into the flask through a side arm of the condenser. The reaction was exothermic and the dropwise addition of nitrile required a period of 0.5 hr. The reaction mixture was then allowed to stand for 1 hr., washed with four 100-ml. portions of water, and dried over anhydrous calcium sulfate. Fractional distillation through a small packed column yielded 50.0 g. (85%) of pure 2,2,2-trifluoroethyl perfluorobutyrimidate, b.p. 93.0–93.5.

Anal. Calcd. for $C_6H_3F_{10}NO$: N, 4.74. Found: N, 4.95.

2,2,2-Trifluoroethyl Perfluoroacetimidate.—Into a heavy-wall glass ampoule of approximately 50-cc. capacity was placed 15.0 g. (0.15 mole) of trifluoroethyl alcohol. The ampoule was cooled with liquid nitrogen and pumped free of air, and 9.50 g. (0.10 mole) of perfluoroacetonitrile and 0.395 g. (0.005 mole) of trimethylamine were added. The ampoule was sealed and allowed to warm to room temperature; the reaction occurred at temperature below 0° as evidenced by the rapid warming of the ampoule. After standing 12 hr., the ampoule was opened and its contents were washed with two 50-ml. portions of water and dried over anhydrous calcium sulfate. Fractional distillation gave 17.5 g. (90%) of pure 2,2,2-trifluoroethyl trifluoroacetimidate, b.p. 58.0–59.0°.

Anal. Calcd. for $C_4H_3F_6NO$: N, 7.18. Found: N, 7.37.

Dimethyl Perfluoroglutarimidate.—Anhydrous methyl alcohol (20.0 ml.) and 0.5 ml. of triethylamine were placed in a 100-ml. flask containing a polytetrafluoroethylene-coated stirring bar. The flask was attached to the vacuum system, cooled with an ice bath, and pumped free of air. Perfluoroglutaronitrile (15.5 g., 0.0767 mole) was brought into contact with the stirred methyl alcohol solution at an average pressure of 75 mm. After approximately 0.5 hr. the nitrile had reacted completely. The reaction product was washed with water and dried over anhydrous calcium sulfate. The infrared spectra of this product (16.95 g.) showed absorption maxima typical of the imidate group. Attempted distillation at atmospheric pressure resulted in the loss of methyl alcohol and apparent polymerization.

Reaction of Perfluorobutyronitrile with Methyl Alcohol in the Presence of Hydrogen Chloride.—In a previously evacuated heavy-wall glass ampoule of approximately 20-cc. capacity were condensed 1.95 g. (0.010 mole) of perfluorobutyronitrile, 0.32 g. (0.10 mole) of anhydrous methyl alcohol, and 0.36 g. (0.010 mole) of anhydrous hydrogen chloride. The ampoule was sealed and allowed to warm slowly; an exothermic reaction occurred at approximately 0°. After standing 24 hr. at room temperature, the ampoule was opened and 0.0095 mole of a gas whose infrared spectra showed the presence of CH_3Cl was collected. The solid remaining in the ampoule was identified by its melting point and infrared spectra as perfluorobutyramide.

Methyl Perfluoroacetothioimidate.—Anhydrous diethyl ether (40 ml.), was placed in a heavy-wall glass ampoule of approximately 100-cc. capacity. The ampoule was cooled in liquid nitrogen and pumped free of air; perfluoroacetonitrile (9.5 g., 0.10 mole), methyl mercaptan (4.8 g., 0.10 mole), and anhydrous hydrogen chloride (3.6 g., 0.10 mole) were condensed in the ampoule. The sealed ampoule was allowed to warm to room temperature slowly over a period of 12 hr., then opened, and diethyl ether and unreacted starting materials were removed under reduced pressure. Remaining in the tube was 13.5 g. of white, solid methyl perfluoroacetothioimidate hydrochloride (76%). A small amount of this hydrochloride was treated with triethylamine in anhydrous ether; removal of the amine hydrochloride by filtration and the solvent ether under reduced pressure

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[16] B. B. Lampert and F. G. Bordwell, *J. Am. Chem. Soc.*, **73**, 2369 (1951).

[17] W. L. Reilly and H. C. Brown, *ibid.*, **78**, 6032 (1956).

left pure methyl perfluoroacetothioimidate, identified by comparison of its infrared spectra with that of an authentic sample.[9]

Isopropyl Perfluorobutyrimidate.—Isopropyl alcohol (15.0 g., 0.25 mole) was placed in a 50-cc. glass ampoule. The ampoule was cooled in liquid nitrogen and pumped free of air. Perfluorobutyronitrile (39.0 g., 0.20 mole) and trimethylamine (0.59 g., 0.01 mole) were condensed in the ampoule which was sealed, slowly warmed to 65°, and held at this temperature for 48 hr. The reaction mixture was then washed with two 100-ml. portions of water and dried over anhydrous calcium sulfate. Fractionation through a packed column gave 44.2 g. (87%) of pure isopropyl perfluorobutyrimidate, b.p. 101.0–101.5°.

Anal. Calcd. for $C_7H_8F_7NO$: C, 32.95; H, 3.16, F, 52.12; N, 5.49. Found: C, 33.06; H, 3.36; F, 51.50; N, 5.13.

Isopropyl Perfluoroacetimidate.—Isopropyl alcohol (9.0 g., 0.15 mole) was allowed to react with perfluoroacetonitrile (9.5 g., 0.10 mole) and trimethylamine (0.59 g., 0.01 mole) as described in the previous preparation. After standing 72 hr. at room temperature and 24 hr. at 70°, the contents of the ampoule were fractionally distilled through a packed column to yield 13.8 g. (89%) of isopropyl perfluoroacetimidate, b.p. 65.5–67.0°.

Anal. Calcd. for $C_5H_8F_3NO$: N, 9.03. Found: N, 8.51.

Attempted Reactions of Perfluoroalkyl Nitriles with Tertiary Alcohols.—Sodium (0.5 g.) was dissolved in 10 ml. of *t*-butyl alcohol; the solution was sealed in a glass ampoule with 9.7 g. (0.05 mole) of perfluorobutyronitrile. After the ampoule had been heated at 70–75° for 24 hr., it was opened and 3.2 g. (0.0164 mole) of perfluorobutyronitrile was recovered. The liquid remaining in the ampoule, 5.65 g., was shown by its infrared absorption spectra to be 2,4,6-tris(perfluoropropyl)-1,3,5-triazine. The conversion was 58%.

In a similar manner perfluorobutyronitrile (9.7 g.) was heated at 75° for 48 hr. with 0.59 g. of trimethylamine and 10.0 ml. of *t*-butyl alcohol in a sealed ampoule. This reaction produced 9.45 g. (97%) of crude 2,4,6-tris(perfluoropropyl)-1,3,5-triazine.

The reaction of perfluorobutyronitrile was also attempted with 1,1-dimethylheptafluorobutyl alcohol. A solution of 0.05 g. of sodium in 6.85 g. (0.03 mole) of 1,1-dimethylheptafluorobutyl alcohol was sealed in a 30-cc. glass ampoule with 5.85 g. (0.030 mole) of perfluorobutyronitrile and heated at 70–75° for 32 hr. Examination of the infrared spectra of the liquid mixture showed the characteristic strong absorption band at 6.47 μ of the perfluoroalkyl-substituted 1,3,5-triazine. The characteristic imidate band at 5.9–6.0 μ was absent. Attempted reaction of perfluoroacetonitrile with *t*-butyl alcohol using trimethylamine as a catalyst under similar conditions resulted only in conversion of the nitrile to 2,4,6-tris(perfluoromethyl)-1,3,5-triazine.

Phenyl Perfluorobutyrimidate.—Phenol (9.4 g., 0.10 mole) and 0.07 g. of sodium were dissolved in 20 ml. of anhydrous dioxane. This solution was sealed in a 60-cc. glass ampoule with 19.5 g. (0.10 mole) of perfluorobutyronitrile and heated at 50° for 33 hr. The reaction mixture was washed with two 100-ml. portions of water and dried over anhydrous calcium sulfate. Distillation at reduced pressure (11 mm.) through a packed column gave 22 g. of slightly yellow and impure phenyl perfluorobutyrimidate.

With this same procedure, but with 0.59 g. of trimethylamine instead of phenoxide ion as catalyst, this reaction resulted in excellent crude yields of phenyl perfluorobutyrimidate; however, all attempts at distillation of the trimethylamine-catalyzed product were unsuccessful and resulted in decomposition to phenol and perfluorobutyronitrile.

An analytical sample of phenyl perfluorobutyramidate was prepared by repeated vacuum distillation until a clear, colorless liquid with a constant boiling point of 61–62° (6 mm.) was obtained.

Anal. Calcd. for $C_{10}H_6F_7NO$: F, 45.99; N, 4.81. Found: F, 45.80; N, 4.96.

A pure sample of phenyl perfluorobutyramidate, after standing for 4 months at room temperature, separated into two layers. Infrared spectra of the lower layer indicated relatively pure 2,4,6-tris(perfluoropropyl)-1,3,5-triazine.

The reaction of phenol with perfluorobutyronitrile using hydrogen chloride as a catalyst was attempted by sealing the reactants in an ampoule and heating the mixture at 45° for 24 hr. The contents of the ampoule was then added to 100 ml. of water; the liquid products were separated and dried over anhydrous calcium sulfate. The infrared spectra of the product (9.5 g.) showed that it was 2,4,6-tris(perfluoropropyl)-1,3,5-triazine.

O-(Perfluoroacetimidoyl)propanone Oxime.—Propanone oxime (5.0 g., 0.0685 mole) was dissolved in 20 ml. of anhydrous ether and the solution was sealed in a 50-cc. glass ampoule with 9.5 g. (0.10 mole) of perfluoroacetonitrile. After standing at room temperature for 48 hr., the ampoule was opened and unreacted perfluoroacetonitrile and ethyl ether were removed under reduced pressure. The clear liquid product was distilled under reduced pressure to give 11.0 g. (96%) of O-(perfluoroacetimidoyl)propanone oxime, b.p. 38° (6 mm.).

Anal. Calcd. for $C_5H_7F_3N_2O$: N, 16.55. Found: N, 16.25.

O-(Perfluorobutyrimidoyl)perfluoropropanone Oxime.—By a procedure that was identical with the one described above for the preparation of O-perfluoroacetimidoylpropanone oxime, perfluorobutyronitrile (9.7 g., 0.050 mole) was allowed to react with 3.6 g. (0.050 mole) of propanone oxime in 20 ml. of anhydrous ethyl ether in a 40-cc. glass ampoule. Fractionation of the liquid product through a small packed column gave 12.5 g., b.p. 55.0–56.0 (7 mm.), of pure O-(perfluorobutyrimidoyl)propanone oxime.

Anal. Calcd. for $C_7H_7F_7N_2O$: C, 31.35; H, 2.63; F, 49.60; N, 10.47. Found: C, 31.54; H, 2.65; F, 49.20; N, 10.81.