Anal. Calcd for $C_8H_6F_3ON$: C, 50.8; H, 3.18; F, 30.2. Found: C, 50.2; H, 3.21; F, 30.03.

Registry No.—CF_3COSH, 2925-25-9; CF_3COSCl, 21690-85-7; CF_3COSBr, 21690-86-8; $(CF_3COS)_2$, 21690-87-9; $(CF_3COS)_2Hg$, 21690-88-0; $CF_3COSH \cdot C_5H_5N$, 21690-89-1; $CF_3COSH \cdot C_6H_7N$, 21690-90-4; $CF_3COSCH_2CH_3$, 383-64-2.

Acknowledgment.—We wish to thank Mr. B. Nist of the University of Washington for obtaining the fluorine nmr spectra and Dr. A. Levinson for obtaining the proton spectra. We are indebted to the Huffman Laboratories, Inc., for the chemical analysis. A special acknowledgment is given to Mr. L. Kegley, who first prepared CF_3COSBr and helped in preparing CF_3COSH.

Fluoronitromethane. Synthesis and Estimation of Acid Strength[1]

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The effect of α-fluorine substitution on carbon acidity has been the subject of several recent reports.[2-5] The conclusion has been accepted that the great acid strengthening effect of α-fluorine essentially disappears when effective –R substituents are also present on the same carbon atom. That is, α-F does not stabilize planar carbanions, but only pyramidal ones. We now report the first synthesis and our studies of fluoronitromethane, IV, the simplest member of the series studied by Adolph and Kamlet.[4] Understanding of IV has been delayed by its unexpected instability toward base. We find IV to have p$K_a \approx 9.55$, as compared with 10.22 for nitromethane,[6] in essential agreement with the work cited.

Fluoronitromethane (IV) was prepared by saponification and decarboxylation of diethyl fluoronitromalonate (II), eq 3, synthesis of which from diethyl malonate,

$$CH_2(CO_2Et)_2 + HNO_3,\ 90\% \xrightarrow{15^\circ} \underset{\textstyle I}{O_2N\text{—}CH(CO_2Et)_2} \quad (1)$$

$$I + NaH + FClO_3 \xrightarrow{DMF} \underset{\textstyle II}{O_2N\text{—}CF(CO_2Et)_2} \quad (2)$$

$$II \xrightarrow[EtOH]{NaOH} \underset{\textstyle III}{[O_2N\text{—}CF(CO_2Na)_2]?} \xrightarrow[H_2O]{ClCH_2CO_2H} \underset{\textstyle IV}{FCH_2NO_2} \quad (3)$$

eq 1 and 2, has been described.[7] Yields from II ranged from 5 to 32%. The crucial step appears to be the neutralization of the difficultly characterizable III. The product was characterized by elemental analysis and spectra (*cf.* Experimental Section).

The preparation of 1-fluoro-1-nitroethane has been achieved in 5% yield, by reaction of the aqueous nitronate salt with fluorine gas.[8] Under similar conditions, the yield of IV would likely be less than 5%, since less acidic nitro compounds gave poorer yields, and nitromethane is less acidic than nitroethane.[6]

Fluoronitromethane proved sufficiently unstable to base that only an approximate determination of pK_a was feasible by titration. Spectrophotometry at low pH failed because a suitable ultraviolet absorption maximum for the conjugate base was not found. It was possible to measure the rates of base-catalyzed hydrogen–deuterium exchange of nitromethane and IV and thus to estimate a pK_a value which agreed with the titrimetric one.

Addition of more than 10% of the theoretical amount of base, pH rising above *ca.* 9.0, was accompanied by a downward drift of pH at *ca.* 0.1 unit/min. The drift ceased when the pH exceeded 10.7, roughly the equivalence value. Even if a titration was carried out rapidly, and the solution quickly neutralized, only a trace of IV was recovered. IV was quantitatively recovered from 0.1 *N* hydrochloric acid and pure water, and after titration to pH 8.7; decomposition was slight in a Borax buffer (pH 9.18) in 2 min. Excess 0.1 *N* or 1.0 *N* base decomposed IV rapidly and completely, and 60–65% yields of fluoride ion could be detected, using a fluoride electrode and standard fluoride solutions. Nitrite ion could also be detected in *ca.* 50% yield by treatment with sulfamic acid and gravimetric determination of the resulting sulfate as barium sulfate. The fate of the carbon atom of IV remains unknown: no other product was extracted into dichloromethane, carbonate was not precipitated, and formaldehyde was not detected using 2,4-dinitrophenylhydrazine. Our feeling is that base-catalyzed dimerization such as that reported for 1-chloro-1-nitroethane and -propane was taking place.[9]

A rough determination of pK_a was made by rapid titration with 0.100 *N* base. The results are shown in Table I. Only in runs 3 and 4 were clean equivalence breaks observed. Our interpretation of the titrations depends on the exchange rates reported below. Thus, it may be calculated that neutralization has $t_{1/2} = 8$ sec at pH 10 (assuming that it is the rate-determining step of hydrogen isotope exchange). The meter never reads the maximum pH, corresponding to addition of 0.5 ml of 0.1 *N* base, because of neutralization, and the maximum (runs 1 and 2) has no significance. The initial rapid drop thus reflects neutralization, and the persistent slow drop, probably decomposition. Runs 3–5 yield a pK_a value of 9.55 ± 0.1, not much less than that of nitromethane,[6] 10.22.

Results of two measurements of the rates of base-catalyzed hydrogen–deuterium exchange of IV and nitromethane are given in Table II. These were performed at pH 8.0, since a run at pH 8.5 gave nearly complete exchange in 9 min and a serious drop in pH for IV. Observed rate constants were divided by the number of exchangeable protons and the corrected constants entered in Table II. The agreement is better

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TABLE I

POTENTIOMETRIC TITRATIONS OF FLUORONITROMETHANE

Base, ml	pH Run 1	Run 2	Run 3	Run 4	Run 5
0.0	3.90	3.90	4.00	4.03	4.43
0.5	8.65	8.63	8.65	8.62	8.63
1.0	9.02	9.04	9.03	9.02	9.03
1.5	9.30	9.34	9.25	9.25	9.30
2.0	9.55	9.58	9.40	9.43	9.40
2.5	9.75	9.85	9.58	9.58	9.60
3.0	9.95	10.08	9.70	9.70	9.80
3.5	10.21	10.18	9.78	9.90	10.0
4.0	10.42	10.42	9.94	10.05	10.4
4.5	10.70	10.65	10.24	10.30	10.8
5.0	11.03	11.00	10.62	10.68	11.2
5.5	11.39	11.39	11.01	11.04	11.45
6.0	11.46	11.45	11.25	11.27	
6.5	11.57	11.56	11.40	11.42	
7.0	11.64	11.63	11.52	11.53	
pK_a	9.75	9.77	9.55	9.55	9.5 ± 0.1

TABLE II

HYDROGEN ISOTOPE EXCHANGE OF IV AND NITROMETHANE

Run	Compound	pH Initial	pH Final	Time, min	Exchange, % Found	Exchange, % Equil	Rate constant for exchange, per H, M^{-1} min^{-1}
1	CH_3NO_2	8.00	7.90	5.0	9.7	91.8	$0.6\ (\pm\ 0.1) \times 10^4$
1	FCH_2NO_2	8.00	7.50	5.0	15.2	93.4	$2.5\ (\pm\ 0.5) \times 10^4$
2	CH_3NO_2	8.0	7.90	10.0	13.6	91	$0.55\ (\pm\ 0.1) \times 10^4$
2	FCH_2NO_2	8.0	7.90	10.0	32.2	94	$2.3\ (\pm\ 0.5) \times 10^4$

than might be expected. Fluoronitromethane exchanges only four times more rapidly than nitromethane, and application of the Brønsted Catalysis Law in the form of eq 4 ($\beta \leq 1.0$) yields p$K_a \leq 9.6$ for IV. This value

$$\frac{1}{\beta}\log(k_2/k_1) = pK_1 - pK_2 \qquad (4)$$

is in close but perhaps fortuitous agreement with our rough titrimetric value. Although the correlation in this way of kinetic acidity and pK_a frequently succeeds, one must be mindful of notable failures; thus, acetylene and phenylacetylene differ by some 6 pK_a units in thermodynamic acidity, but exchange at nearly identical rates.[10]

The similarity of the acidities of IV and nitromethane supports the generalization that α-fluorine fails to stabilize planar carbanions. It is interesting to note that the reported pK_a[11] of difluoronitromethane is 12.4; the conflict between the inductive effect of an α-fluorine and the –R effect of nitro has become very serious.

Experimental Section

Spectra.—Infrared spectra were recorded on a Perkin-Elmer Model 137 or 237 instrument, and wavelengths calibrated *vs.* polystyrene film. Nmr spectra were recorded on a Varian A-60 spectrometer.

Diethyl Nitromalonate (I).—The preparation was carried out exactly as prescribed by Weisblat and Lyttle.[12] From 80.0 g (0.50 mol) of diethyl malonate (previously distilled, bp 56° (0.5–1.25 mm) and 276 g (3.95 mol) of 90% nitric acid, with a reaction time of 2.5 hr at 12–19° and 2.5 hr at 19–26°, there was obtained after distillation in four fractions 85.1 g (0.415 mol, 83%) of material with bp 94.0–96.0° (0.5–1.0 mm) and infrared (CCl_4) 3.30 (w), 5.67 (s), 6.36 (s), 6.8–6.9 (w), 7.3–7.4 (m), 7.7 (s), 8.0 (m), 8.3 (m), 8.5–8.7 (m), 9.2 (w), 9.7 (s), 11.7 μ (w).

Diethyl Fluoronitromalonate (II).—The preparation of II in 70% yield from I and $FClO_3$ is reported by Freeman[7] with few details. A 500 ml three-necked round-bottomed flask was fitted with a gas inlet tube (a distillation adapter fitted with a standard taper joint and stopcock), pressure equalized dropping funnel, and reflux condenser connected to a gas bubbler containing CCl_4. Sodium hydride (4.8 g, 0.20 mol, as a 52% suspension in mineral oil, total weight 9.6 g) was placed in the flask and washed with hexane, the hexane decanted, 200 ml of reagent grade dimethylformamide added, and the solution purged with nitrogen. Then diethyl nitromalonate (I), 41.0 g, 0.20 ml, was added during 30 min, smooth evolution of hydrogen being revealed by the bubbler. The intensely reddish yellow solution was cooled to 15° and purged with nitrogen for 1 hr. Perchloryl fluoride (Pennsalt Chemicals, kindly provided by Professor Walter J. Gensler) was admitted from a weighed 1-lb lecture bottle during 3 hr, while the solution was vigorously stirred magnetically, at such a rate that very little gas escaped the bubbler. The solution rapidly became warm if the cooling bath was removed. The color had faded to pale yellow in 2 hr. In all 24.0 g (0.23 mol) perchloryl fluoride was admitted. After standing for 2 days at ambient temperature, the solution was poured into 1 l. of water and extracted with dichloromethane in portions of 200, 100, and 100 ml. The organic extracts were washed with water, dried with sodium and magnesium sulfate, and filtered, and the dichloromethane was stripped on the rotary evaporator. Distillation of the residue gave colorless liquid in three fractions: 1, 2.99 g, bp 57–80° (0.7 mm); 2, 24.97 g, bp 80–81° (0.65 mm); 3, 5.85 g, bp 82–87° (0.7 mm). The total yield was 33.81 g, 0.152 mol, 76% of theory. Fraction 1 colored 0.01 *N* aqueous base yellow on shaking (presence of I), while fraction 2 did not. Fraction 1 was also found by nmr to contain DMF: infrared (CCl_4) 3.33, 3.38 (w), 5.61 (s), 6.28 (s), 6.8, 6.9 (doublet, w), 7.3, 7.4 (doublet, w), 7.8 (s, broad), 8.4 (s, sharp), 9.30 (s, sharp), 9.7–9.9 (w), 11.7 μ (m).

Disodium Fluoronitromalonate (III).—Diethyl fluoronitromalonate, 223 g, 1.0 ml, was saponified in four portions, according to the following procedure. Sodium hydroxide, 37 g, 0.925 mol, was dissolved in 50 ml of water; the solution was dissolved in 400 ml of absolute ethanol and cooled in an ice bath. Ester II, 50.0 g, 0.224 mol, in 100 ml of absolute ethanol, was added slowly to the stirred base. The white solid which precipitated rapidly was periodically collected by suction filtration, washed with absolute ethanol, then dichloromethane, and air dried. After the last portion of ester had been added, the solid was collected immediately; no solid which precipitated subsequently was collected. The fine white powder weighed 50.0 g (theoretical yield of disodium fluoronitromalonate, 47.3 g). The total yield of solid from four portions of ester was 217.5 g.

Fluoronitromethane (IV).—The solid from saponification of II was completely decomposed by ice-cold dilute hydrochloric acid, and dichloromethane extracts showed no infrared absorption.

The salt, 100 g (0.475 mol if pure III), was dissolved in 750 ml of water and the solution cooled in an ice bath. A solution of chloroacetic acid, 90 g, 0.95 ml, in 1 l. of water was added slowly from a buret with vigorous stirring until the pH had decreased to 4.5. About 950 ml of acid solution was required, and the addition required about 3 hr. Effervescence began after about one-third of the acid had been added. The solution did not oxidize potassium iodide unless the pH was allowed to decrease to 3.4. The resulting solution was combined with that from the acidification of 111.7 g of salt and extracted with three 600-ml portions of dichloromethane. The solvent was distilled through a Snyder column (bp 39–42.0°), the column was removed, and the product was distilled, bp 57–62° (125–130 mm), yield 25.1 g, 0.317

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mol; the per cent yield from 211.7 g of salt (1.00 mol if pure) and 190 g of acid (2.0 mol) was 32%. The product, a colorless liquid, was stable indefinitely; stored at 0–5°, it did not etch the glass vessel or develop an acid odor, but retained an odor milder than that of nitromethane. It was sparingly soluble in water and CCl_4: infrared (CH_2Cl_2) 6.27 (s), 7.27, 7.37 (doublet, m), 8.8 μ (s); nmr ($CHCl_3$) δ 5.68 ppm (doublet, J = 46.0 cps).

The spectra of nitromethane follow: infrared (CH_2Cl_2) 6.40, 7.20, 7.30 μ (doublet), *inter alia* [These are shifted in IV in the expected directions;[13] nmr ($CHCl_3$) δ 4.32 ppm (singlet)].

The nmr spectrum of bromonitromethane ($CHCl_3$) had δ 5.60 ppm (singlet).

Anal. Calcd for CH_2NO_2F: C, 15.20; H, 2.55; N, 17.72; mol wt, 79.03. Found (MIT Microanalytical Laboratory): C, 15.17; H, 2.76; N, 17.71. Found (Schwarzkopf Microanalytical Laboratory): C, 14.54; H, 3.05; N, 16.85.

Titration of IV with Standard Base.—Solutions of IV, 0.100 *N*, 5-ml aliquots, were titrated with standardized 0.100 *N* sodium hydroxide using a Beckman Zeromatic SS-3 pH meter standardized with fresh 0.1 *N* Borax solution (pH 9.18). Addition of 0.5-ml aliquots of base to the rapidly stirred solution caused a rapid rise of pH to a maximum followed by a rapid drop for about 3 sec, then a slow decline. In runs 1 and 2, Table I, the maximum was read; in runs 3 and 4, the value after cessation of the rapid drop. In run 5, at the suggestion of a referee, given amounts of base were added all at once to fresh 5-ml aliquots of IV solution; the meter was read as in runs 3 and 4. Solutions developed both a yellow color and a characteristic sweet odor unlike that of IV, oxides of nitrogen, or formaldehyde. The odor disappeared after 24-hr exposure to air.

A solution resulting from a slower titration was acidified to pH 2.8 with chloroacetic acid and extracted with sufficient dichloromethane to make a 2% solution of IV if recovery were complete. The infrared spectrum showed a trace of IV.

Another titration was carried only to pH 8.70, then treated as above. The infrared spectrum of the extract showed that some 50% of IV had been recovered.

Spectrophotometry of IV in Basic Buffers.—Solutions of IV in pure water and in buffers were examined using quartz cells in a Cary 14 UV-Vis spectrophotometer. Solution in pure water showed only end absorption. In 0.125–0.16 *M* phosphate and borate buffers of pH 6.6–9.45, a broad absorption with λ_{max} 380 mμ appeared, reaching a maximum absorbance at pH 8.24 and remaining constant for at least 1 hr. This is attributed to an impurity.

Recovery of IV from Aqueous Solutions.—IV, 0.079 g (1.0 mol), was dissolved in 50 ml of 0.1 *M* Borax, pH 9.18; after 2 min the solution was acidified to pH 4 with chloroacetic acid and extracted with 4 ml and 3 ml portions of dichloromethane. The infrared spectrum of the extract showed IV; by comparison with a standard, the recovery was found to be 50%. Similar experiments using buffers initially of pH 8.7 allowed recovery of more than 50% of IV.

A solution of 79 mg of IV in 20 ml of 0.1 *N* HCl was allowed to stand 5 min and then shaken with 5 ml of CH_2Cl_2. The infrared spectrum showed a nearly complete recovery of IV by comparison with a standard.

Nmr Spectra of Basic Solutions of IV.—To 1 ml of a 3 *N* buffer of tris(hydroxymethyl)aminomethane and sulfuric acid at pH 9.0 was added 79 mg of IV; the solution was shaken and its nmr spectrum immediately recorded. The doublet characteristic of IV was evident and decreased 50% in intensity in a few minutes. A solution of IV in 3 *N* sodium hydroxide showed no absorption at all for IV.

Base-Catalyzed Hydrogen–Deuterium Exchange of IV and Nitromethane.—Approximately 2-g samples of IV and nitromethane were added to 20–25 ml of buffers prepared in D_2O, which were stirred for specified times and then acidified to pH 5 with chloroacetic acid. The solutions were extracted with 20 ml of dichloromethane and the extracts washed twice with H_2O; most of the solvent was distilled through a Snyder column. Traces of water were thus removed as the dichloromethane azeotrope. The residue was analyzed by glpc using known mixtures of dichloromethane and nitro compound as standards. Aliquots of the residues were sealed into dried glass tubes and submitted to Mr. Josef Nemeth for total deuterium analysis by the combustion and falling drop method. The per cent exchange by the nitro compound could easily be calculated. The buffer used consisted typically of 3.04 g, 25.0 mmol, of tris(hydroxymethyl)aminomethane in 14 ml of D_2O and enough of a solution of 1.26 g of 96% H_2SO_4 in 14 ml of D_2O to bring the pH to the desired value (8.5 or 8.0) before addition of nitro compound. Typical raw data appear in Table III.

TABLE III

TYPICAL ANALYSIS OF MIXTURES OF CH_3NO_2 AND FCH_2NO_2 WITH CH_2Cl_2

Compound	Wt % from glpc	Total atom % excess *d*
CH_3NO_2	41.0	4.95
CH_2FNO_2	54.5	8.30

Approximate second-order rate constants for exchange were calculated assuming that the reactions were pseudo first order and specific base catalyzed. For nitromethane in both runs and for IV in run 2, the concentration of OH^- was assumed constant at 0.9×10^{-6} *M*. For IV in run 1, the pH was treated as a step function, decreasing 0.1 unit each minute; the reported rate constant reproduces the observed extent of exchange.

Registry No.—I, 603-67-8; II, 680-42-2; III, 21824-09-9; IV, 21824-10-2.

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Stereochemistry of Acid-Catalyzed Hydride Transfer to Cyclic Alkenes

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Though electrophilic additions to alkenes usually proceed with *trans* stereochemistry,[2] a number of exceptions to this generalization have been noted. Hammond and his students first observed that, though hydrogen bromide added exclusively *trans* to 1,2-dimethylcyclohexene, acid-catalyzed hydration gave approximately equal amounts of *cis* and *trans* alcohols.[3] Dewar and Fahey have shown that addition of deuterium bromide to alkenes which afford benzylic carbonium ions (acenaphthylene, indene, 1-phenylpropene) occurs predominantly *cis*,[4] and addition of DBr even to cyclohexene has been reported to yield significant amounts of *cis* adduct.[5] Some *cis* addition of chlorine results with aryl-substituted alkenes,[6] and *cis* addition of

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