Reactions of N-Fluoriminonitriles[1]

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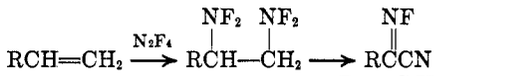
The conversion of N-fluoriminonitriles **1a**, **b**, and **c** into imidates and α-fluorimino esters is reported. Grignard reagents and the fluoriminonitriles give both cleavage and fluorine-substitution reactions. The nitrile function of fluoriminonitriles will participate in 1,3-dipolar cycloaddition with 2,4,6-trimethylbenzonitrile oxide.

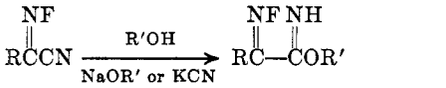
The addition of tetrafluorohydrazine to terminal olefins[2] followed by dehydrofluorination[3] of the 1,2-bis(difluoramino)alkanes produced, provides a straightforward route to N-fluoriminonitriles (**1**). In a detailed report on the preparation of fluoriminonitriles,[3] only the chemistry of 1-cyano-N-fluoroformimidoyl fluoride (**1**, R = F) was investigated in detail. Another



1a, R = C_6H_5
b, R = 4-ClC_6H_4
c, R = *n*-C_4H_9-O-

publication[4] reported briefly on the fragmentation and rearrangement of **1a** and **b** in the presence of alkoxides. This paper reports additional study of the fluorimines **1a–c**.

Because of the tendency of **1a** and **b** to cleave to aromatic nitrile and rearrange to a dialkoxy imidocarbonate in the presence of sodium alkoxides,[4] it was of interest to attempt imidate formation from these α-fluoriminonitriles by the standard base-catalyzed methods.[5] Nucleophilic attack at the nitrile function of **1a** or **b** possibly is responsible for the fragmentation reaction. The interaction of **1a** and **b** with methanol containing a catalytic amount of sodium methoxide, or with potassium cyanide in refluxing methanol, gave the corresponding imidates **2a** and **b**. Some nitrile, the cleavage product, was formed in the preparative runs.



2a, R = C_6H_5; R′ = CH_3
b, R = 4-ClC_6H_4; R′ = CH_3
c, R = *n*-C_4H_9-O-; R′ = CH_3

Since the equilibrium between nitrile and imidate was established rapidly, and was overwhelming in favor of the imidate (as evidenced by ^{19}F nmr spectra), the low-temperature, methoxide-catalyzed route to **2a** and **b** was preferable. Characterization of the methyl imidates is summarized in Table I.

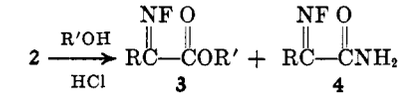
Upon exposure to aqueous alcoholic hydrochloric acid, the imidates smoothly hydrolyzed to α-fluorimino esters **3**. The ethyl imidates of **1a** and **b** were prepared and hydrolyzed directly in the ethanolic reaction mixture. Small amounts of α-fluoriminoamides **4** accompanied the esters **3** prepared by this procedure. The amides apparently were a result of the hydrolysis step, since they were not detected (by ^{19}F nmr) prior to this step. Table II summarizes the properties of the α-fluorimino esters **3**.

TABLE I

METHYL α-FLUORIMINOIMIDATES

R	^{19}F nmr, ϕ[a]	Anal., % Calcd C	Calcd H	Calcd N	Found C	Found H	Found N
C_6H_5	−27.3	59.99	5.03	15.55	60.24	4.81	15.22
4-ClC_6H_5	−28.3	50.36	3.76	13.06	49.98	3.35	13.81
n-C_4H_9-O- (*syn*)[b]	+47.7	47.72	7.44	15.90	47.91	7.61	15.52
(*anti*)	+38.2	47.72	7.44	15.90	46.74	7.07	15.40

[a] ϕ values are measured in parts per million (ppm) from internal CCl_3F. [b] F and O *cis*.



a, R = C_6H_5; R′ = CH_3
b, R = 4-ClC_6H_4; R′ = CH_3
c, R = *n*′C_4H_9-O-; R = CH_3

TABLE II

α-FLUORIMINO ESTERS

R	R′	^{19}F nmr, ϕ[a]	Anal., % Calcd C	Calcd H	Calcd N	Found C	Found H	Found N
C_6H_5	CH_3	−27.7	59.66	4.45	7.73	59.31	4.48	7.94
C_6H_5	C_2H_5[b]	−28.2	61.53	5.16	7.18	62.01	5.49	7.09
4-ClC_6H_4	CH_3[c]	−30.0	50.13	3.27	6.49	50.10	3.27	6.65
4-ClC_6H_4	C_2H_5[d]	−29.0	52.30	3.95	6.10	52.26	3.93	6.32
C_4H_9-O- (*syn*[e])	CH_3	+48.4	47.45	6.83	7.90	47.48	7.12	8.00
C_4H_9-O- (*anti*)	CH_3	+30.6	47.45	6.83	7.90	47.62	6.72	7.73

[a] ϕ values are measured in parts per million (ppm) from internal CCl_3F. [b] Calcd: F, 9.7. Found: F, 9.8. [c] Mp 34–36°. [d] Mp 35–37°. [e] F and O *cis*.

Fluorimines **1a** and **b** apparently exist mainly in the *anti* form, although some *syn* isomer is present in the usual samples.[3,4] However, imidates **2a** and **b**, and fluorimino esters **3** derived from **1a** and **b**, apparently were isolated in only one configuration; only one sharp ^{19}F nmr resonance peak was observed with each sample. Since the starting configuration is presumed to be *anti* (aromatic ring and fluorine *trans*) and because the *syn* isomers may well be prone to cleavage *via* a *trans* fragmentation process, imidates **2a** and **b** and the corresponding esters **3** are assumed to be the *anti* isomers.

Fluorimine **1c**, a mixture of *syn* and *anti* isomers, did not rearrange or fragment when treated with an equivalent or an excess of sodium methoxide in methanol. Instead, displacement of the cyano function occurred,

(1) This research was carried out under the sponsorship of the U. S. Army Missile Command, Redstone Arsenal, Ala., under Contract DAAH01-67-C-0655.

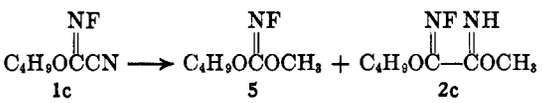
(2) R. C. Petry and J. P. Freeman, *J. Org. Chem.*, **32**, 4034 (1967).

(3) A. L. Logothetis and G. N. Sausen, *ibid.*, **31**, 3689 (1966); A. L Logothetis, U. S. Patent 3,215,709 (Nov 2, 1965).

(4) T. E. Stevens, *J. Org. Chem.*, **32**, 670 (1967).

(5) F. C. Schaeffer and G. A. Peters, *ibid.*, **26**, 412 (1961).

and the fluorimino carbonates **5**, *syn* and *anti*, were produced cleanly. With a catalytic amount of sodium methoxide at −10°, mixtures of **5** and **2c** were produced. A typical reaction mixture, after 15 min or 1 hr at −10°, contained, according to the ^{19}F nmr spectrum, about 7% **1c**, 25% **5**, and 69% the isomers of **2c**. The isomers of **2c** reported in Table I were isolated by vpc from the reaction mixtures.[6] The fluorimino esters **3** (Table II) formed from **2c** were also obtained by vpc of the mixture resulting from acidic hydrolysis of these methanolic solutions. Fluoriminocarbonate **5** hydrolyzed to methyl butyl carbonate under these conditions.

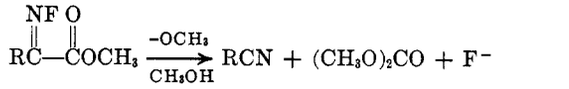


If one makes certain assumptions in assigning structures to the isomers of **1c**, the configuration of imidates **2c** and esters **3c** follows. It seems reasonable to assume that the *anti* isomer, with the F and CN functions adjacent, would have ^{19}F nmr peaks at lower field; this is consistent with earlier assignments in related molecules.[3] Also, the $-CH_2-O-$ protons of the *n*-butoxy group should be most shielded when the fluorine atom is adjacent to it (*syn* isomers); this fluorine, at least, appears to be the most likely part of these molecules to cause a large chemical shift in the protons. Thus, one concludes that **1c**, with a ^{19}F nmr peak at ϕ +23 and the methylene proton resonance at τ 5.83, has the *syn* configuration. The *anti* isomer has ^{19}F resonance at ϕ +8, and the methylene proton peaks are at τ 5.62. Fluoriminoimidate **2c**, with a fluorine peak at ϕ +47.7 and the specific proton peak at τ 6.06, is the *syn* isomer; the *anti* isomer has nmr peaks at ϕ +38.2 and τ 5.72. Along the same line, ester **3c**, characterized by ϕ + 48.4 and τ 5.82 peaks is *syn*, while **3c** with ϕ +30.6 and τ 5.65 is *anti*.

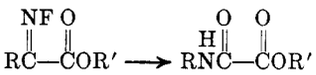
With N-fluoriminocarbonates **5**, there is only a small chemical shift in the ^{19}F nmr spectra. One isomer absorbs at ϕ +89.6, the other at +90. On the basis of the tentative assumptions made for **1c**, the isomer with the +89.6 fluorine peak, and with proton nmr peaks at τ 5.93 for $-O-CH_2-$ and at τ 6.32 for $-O-CH_3$ would have the *anti* $F-C_4H_9-O$ configuration. The *syn* isomer exhibited proton absorption at τ 6.00 for $O-CH_2-$ and 6.22 for CH_3-O-.

The extent to which imidate formation affects the fragmentation and cleavage reactions of **1a** and **b** in alcohols remains unknown. However, both fluorimino-nitrile **1b** and fluoriminoimidate **2b** gave the same ratio of nitrile to imidocarbonate when exposed, under identical conditions, to excess sodium methoxide in methanol. By vpc, 4-chlorobenzonitrile[7] (65%) and dimethyl N-(4-chlorophenyl)imidocarbonate (35%) were formed from each. While **1a** and excess sodium methoxide produced benzonitrile (61%) and dimethyl N-(phenyl)imidocarbonate (39%), **2a** gave 48% nitrile and 52% imidocarbonate. There appears to be little doubt, however, that the fragmentation of the fluoriminonitriles arises from attack by base at the nitrile function of the *syn*-fluorimine.[4]

Fluorimino esters **3a** and **b** were readily cleaved by sodium methoxide in methanol. Only the nitrile, and presumably, dimethylcarbonate were produced; there was no sign of any rearrangement product here.



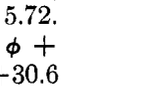
With concentrated sulfuric acid at room temperature, fluorimino esters **3a** and **b**, as well as the related ethyl esters, underwent a clean Beckmann rearrangement to produce esters of oxanilides. Examples are given in the Experimental Section. Fluoriminonitriles **1a** and **b** also undergo a Beckmann rearrangement in warm sulfuric acid.[4]



When treated with Grignard reagents, fluorimines **1a** and **b** were converted into N-substituted α-iminoacetonitriles **6** in low yield. These reactions are summarized in Table III. Fragmentation of the fluoriminonitriles to aromatic nitrile accounted for much of **1a** and **b** in each reaction, although some fluoriminonitrile was usually recovered even with an excess of Grignard reagent. Fluorimine **1c** and the Grignard reagents (*n*-butyl, phenyl) used did not interact.

TABLE III

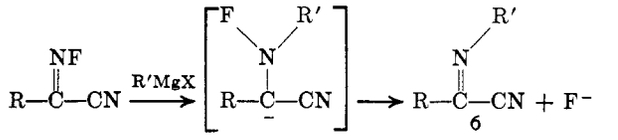
N-SUBSTITUTED α-IMINOACETONITRILES



R	R′	Yield, %	Anal, % Calcd C	Calcd H	Calcd N	Found C	Found H	Found N
C_6H_5	*n*-C_4H_9	18	77.38	7.58	15.0	77.35	7.86	14.8
C_6H_5	C_6H_5[a]	19	81.53	4.89	13.6	81.30	4.77	13.5
4-ClC_6H_4	*n*-C_4H_9	13	64.30	5.94	12.7	65.42	6.22	12.8
4-ClC_6H_4	C_6H_5[b]	18	69.86	3.77	11.6	69.63	3.75	11.8

[a] Mp 70°; F. Barrow and F. J. Thorneycroft [*J. Chem. Soc.*, 769 (1939)] reported 71°. [b] Mp 105°; U. Bellavita [*Gazz. Chim. Ital.* **65**, 899 (1937); *Chem. Abstr.*, **30**, 3420 (1936)] reported 108°.

Although a radical process could account for the low yield of the iminonitriles **6**, ionic addition of the anion



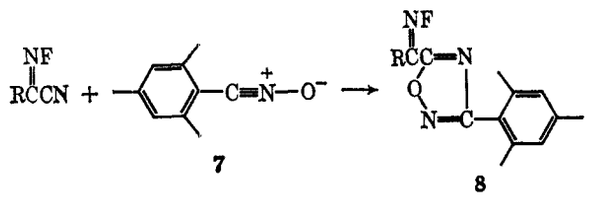
from the Grignard reagent to the >C=N— bond, as sketched, also appears to be a reasonable process. Cleavage probably results from attack of organometallic at the nitrile function. No definitive sign of valeronitrile could be found in the reaction with the *n*-butyl Grignard reagents, but small amounts of benzonitrile were detected (vpc) from reaction of **1b** and the phenyl Grignard reagent.

Using 2,4,6-trimethylbenzonitrile oxide (**7**) as the 1,3-dipole, 1,3-cycloadditions with the N-fluorimino-

(6) A detailed, kinetic study of the reactions of **1c** will be reported by Dr. F. A. Johnson of these laboratories. In this report, the configurations and interconversions of **1c**, **2c**, and **5** will be reported in detail. However, it was established that the same mixtures of isomers of **5** resulted from either isomer of **1c**; the ratio of **2c** to **5** did depend upon the configuration of **1c**.

(7) Some of which was present as the methyl imidate.[5]

nitriles was explored briefly.[8] The progress of the addition could be monitored easily by ^{19}F nmr, and, in ether solution, formation of the 1,2,4-oxadiazole **8** was



7 **8**

complete after 3 days with fluorimines **1a**, **b** and with the *n*-butyl fluorimine **1**, R = C_4H_9. Formation of the oxadiazole from **1c** and **7** was complete after 2 days. Properties of the adducts **8** are summarized in Table IV.

TABLE IV

3-MESITYL-5-(α-FLUORIMINO)-1,2,4-OXADIAZOLES (**8**)

		Anal, %					
		Calcd			Found		
R	^{19}F,[a] φ	C	H	N	C	H	N
C_6H_5[b]	−42.6	69.89	5.21	13.58	70.05	5.20	13.58
4-ClC_6H_4[c]	−43.2	62.70	4.68	12.19	63.27	4.43	12.26
n-C_4H_9-O-[d]	+24.4, +35.6	62.93	6.60	13.76	63.05	6.67	14.08
n-C_4H_9	−42.0	66.41	6.97	14.52	66.57	7.06	14.57

[a] φ values are measured in parts per million (ppm) from internal CCl_3F. [b] Mp 52–53°. [c] Mp 112–114°. [d] Mixture of *syn* and *anti* isomers.

Since the nitrile band was absent in the infrared spectra of adduct **8**, and the ^{19}F nmr spectra of the adduct exhibited peaks characteristic of the fluorimine function (see Table IV), there is little doubt that the cycloaddition process involved the C≡N rather than the C=N—F function. Only with **1c** were *syn* and *anti* isomers detected.[9]

Experimental Section

Melting points and boiling points are not corrected. ^{19}F spectra were run in carbon tetrachloride solution on a Varian 4300B spectrometer operating at 40 MHz; φ values are measured in parts per million from internal CCl_3F standard. Proton nmr spectra were recorded on a Varian A-60 spectrometer. The N-fluoriminonitriles **1a** and **b** were prepared as described earlier.[4]

Preparation of *n*-Butoxyfluoriminonitrile (1c).—The crude adduct,[2] prepared from 45 mmol of butyl vinyl ether and tetrafluorohydrazine in 100 ml of methylene chloride, was cooled in an ice bath while 18 ml of triethylamine in 50 ml of methylene chloride was added dropwise. The mixture was stirred at 20° for 1 hr and then poured into water. The organic phase was washed with 5% aqueous hydrochloric acid and water. The methylene chloride was removed in the Holzmann column and the residue was distilled in the same column to give 5.0 g (77%) of the *n*-butoxyfluoriminonitrile, a mixture of *syn* and *anti* isomers, bp 40° (4 mm).

Anal. Calcd for $C_6H_9N_2OF$: C, 49.99; H, 6.29; N, 19.44. Found: C, 50.05; H, 6.49; N, 19.57.

The isomers could be separated on a 5-ft silicon (G.E. SF-96) on Chromosorb vpc column at 80°. The major isomer was eluted first; on the basis of the ^{19}F nmr peak at φ +23 it was assigned the *syn* configuration. The minor (*anti*) isomer had ^{19}F resonance at φ +8.

Preparation of *n*-Butylfluoriminonitrile.—The tetrafluorohydrazine adduct of 1-hexene (4 g of olefin) in 150 ml of methylene chloride was maintained at 15° while 22 ml of triethylamine in 100 ml of methylene chloride was added dropwise. After 1 hr at 25° the solution was washed with water and 10% aqueous hydrochloric acid. The residue was distilled to give *n*-butylfluoriminonitrile: bp 46° (15 mm); ^{19}F nmr, single peak at φ −64.2.

Anal. Calcd for $C_6H_9N_2F$: C, 56.23; H, 7.08; N, 21.87. Found: C, 56.21; H, 7.29; N, 21.88.

Reaction of Phenylfluoriminonitrile (1a) and Potassium Cyanide in Methanol.—A mixture of 2.96 g of **1a**, 0.40 g of potassium cyanide, and 40 ml of methanol was heated at reflux for 2 hr. The mixture was poured into water and the organic products were extracted into methylene chloride. The residue obtained upon evaporation of the methylene chloride was chromatographed on silica gel. Elution of the column with pentane–methylene chloride elected 0.34 g of starting material and 0.20 g of benzonitrile. Methylene chloride eluted 2.06 g of the methyl imidate of phenylfluoriminonitrile (**2a**), a yellow oil.

Reaction of 4-chlorophenylfluoriminonitrile (1b) and Potassium Cyanide in Methanol.—A mixture of 3.62 g of **2a**, 0.40 g of potassium cyanide and 40 ml of methanol was refluxed for 2 hr. When the mixture was worked up as described for **1a** and the residue chromatographed on silica gel, 0.24 g of recovered **1b**, 0.59 g of 4-chlorobenzonitrile, and 2.08 g of the methyl imidate of 4-chlorophenylfluoriminonitrile (**2b**) was obtained.

Reaction of *n*-Butoxyfluoriminonitrile (1c) and Sodium Methoxide in Methanol. A. With Excess Sodium Methoxide.—To 0.72 g (5 mmol) of **1c** in 10 ml of methanol was added 4 ml of 1.38 *N* sodium methoxide in methanol. After 2 hr at ambient temperature, methylene chloride was added. The organic phase was washed with water. The ^{19}F nmr spectrum indicated fluorine resonance only at φ +89.6 and +90.0. Chromatography (vpc) on the SF-96 column (80°) indicated only two materials, not the starting **1c** isomers, to be present. A sample of these isomers of butyl methyl fluoriminocarbonate (**5**) was distilled, bp 60° (2 mm).

Anal. Calcd for $C_6H_{12}FNO_2$: C, 48.31; H, 8.11; N, 9.39; F, 12.74. Found: C, 48.28; H, 8.51; N, 10.51; F, 12.22.

The isomers were separated on the SF-96 column at 80°; the first material eluted was the minor isomer (ratio *ca.* 1:2). It had an nmr peak at φ +89.6 ^{19}F.

Anal. Found: C, 47.87; H, 8.16.

The second material eluted, the major isomer, had an ^{19}F nmr spectrum peak at +90.0.

Anal. Found: C, 48.21; H, 8.27.

B. With Catalytic Sodium Methoxide.—To 0.72 g (5 mmol) of **1c** in 3 ml of methanol at −15° was added 0.3 ml of 1.3 *N* sodium methoxide in methanol. After 1 hr at −10°, the reaction mixture was partitioned between methylene chloride and water. The methylene chloride solution contained, by integration of peak areas in the ^{19}F nmr spectrum, 7% **1c** (φ +8 and +23), 60% **2c** (φ +38 and +48), and 24% **5** (φ +89–90). The isomers of **2c**, reported in Table I, were separated on the SF-96 vpc column at 100°. The *syn* isomer (^{19}F nmr spectrum had φ +48) was eluted first; it predominated by a 3:2 ratio.

Reaction of 4-Chlorophenylfluoriminonitrile (1b) and Methanol with Sodium Methoxide.—A solution of 0.91 g of **1b** (5 mmol) in 2 ml of methanol was stirred at −10° while 0.20 ml of 1.3 *N* sodium methoxide in methanol was added. After 1 hr at −10°, the reaction mixture was partitioned between methylene chloride and water. The residue obtained from the organic layer was chromatographed on silica gel. Elution of the column with pentane–methylene chloride (1:1) gave 4-chlorobenzonitrile, 0.03 g, identified by infrared spectrum. Continued elution of the column with methylene chloride and ethyl acetate–methylene chloride (1:9) gave **2b**, 0.88 g (83%).

Hydrolysis of Butyl Methyl Fluoriminocarbonate (5).—A mixture of 0.25 g of **5**, 2 ml of methanol, 1 ml of water, and 0.2 ml of aqueous hydrochloric acid was stirred at 40° for 1 hr. The mixture was then partitioned between methylene chloride and water. The methylene chloride solution contained only butyl methyl carbonate by infrared and proton nmr spectra and by retention time on an SF-96 column at 80°. The authentic sample of butyl methyl carbonate was prepared from butanol and methyl chlorocarbonate.

Preparation of *n*-Butoxyfluorimino Esters (3c).—A 3-g portion of a mixture of **2c** and **5**, prepared by the catalyzed addition of methanol to **1c**, was stirred for 1 hr with 40 ml of methanol, 8 ml of water, and 0.25 ml of concentrated hydrochloric acid. The reaction mixture was partitioned beween methylene chloride and water. The methylene chloride extract, by vpc on a Carbowax 20M column at 105°, contained unhydrolyzed **5** and two new peaks, the isomers of *n*-butoxyfluorimino ester **3c**. Since **5** and the *syn* isomer of **3c** overlapped on this column, the reaction

(8) C. Grundmann and J. M. Dean, *J. Org. Chem.*, **30**, 2809 (1965).

(9) The predominant isomer here was presumably the *syn* isomer with a φ +35.6 ^{19}F nmr spectrum; proton absorption due to CH_2O– was at τ 5.62. The isomer with ^{19}F nmr peak at φ 24.4 had the methylene proton at τ 5.38.

mixture was chromatographed on silica gel. Elution of the column with pentane–methylene chloride (2:1) gave the *syn* isomer of **3c**; its purity was established by vpc. Elution of the column with pentane–methylene chloride (1:1) gave a mixture of **5** and *anti* **3c**. The pure sampe of *anti* **3c** (Table II) was trapped from the Carbowax vpc column.

Preparation of Methyl α-Fluoriminophenylacetate (3c).—A mixture of 1.61 g of the methyl imidate of α-fluoriminoacetonitrile, 20 ml of methanol, 4 ml of water, and 1 ml of concentrated hydrochloric acid was stirred at 40° for 1 hr. The mixture was diluted with water and the organic product then was extracted into methylene chloride. Chromatography of the residue over silica gel gave methyl α-fluoriminophenyl acetate (**3a**), 1.05 g, a clear liquid.

The ester **3a** was prepared directly from **1a** as follows. To 0.74 g (5 mmol) of phenylfluoriminonitrile (**1a**) in 5 ml of methanol at −10° was added 0.3 ml of 1.3 *N* sodium methoxide in methanol. The mixture was stirred at −10° for 30 min; then 2 ml of 6 *N* aqueous hydrochloric acid was added. The mixture was warmed to 40°, then set aside 1 hr; it was then partitioned between methylene chloride and water. The residue obtained upon evaporation of the methylene chloride was taken up in pentane and filtered to remove a solid (0.08 g). The solid, from chloroform–hexane, was α-fluoriminophenylacetamide: mp 116–118°; ^{19}F nmr, single peak at ϕ −23.2 in dimethylformamide solution.

Anal. Calcd for $C_8H_7FN_2O$: C, 57.8; H, 4.25; N, 16.9; F, 11.4. Found: C, 57.4; H, 4.31; N, 16.7; F, 11.4.

The filtrate from the pentane extracted yielded 0.54 g of methyl α-fluoriminophenylacetate (**3a**).

Preparation of Ethyl α-Fluoriminophenylacetate.—To 0.37 g of **1a** in 5 ml of absolute ethanol at −10° was added 2 drops of 4.3 *N* aqueous sodium hydroxide. After 1 hr at −10°, the aqueous hydrochloric acid (1.5 ml, 4 *N*) was added and the mixture was handled as described above. Work-up gave 0.03 g of α-fluoriminoacetamide and about 0.25 g of ethyl α-fluoriminophenylacetate, purified by chromatography on silica gel.

Preparation of Methyl α-Fluorimino-4-chlorophenylacetate (3b) and α-Fluorimino-4-chlorophenylacetamide.—To 0.91 g of 4-chlorophenylfluoriminonitrile (**1b**) in 5 ml of methanol at −10° was added 0.30 ml of 1.3 *N* sodium methoxide in methanol. The mixture was stirred at −10° for 30 min, then 2 ml of 6 *N* aqueous hydrochloric acid was added, and the mixture was warmed at 40° for 15 min. After cooling, the reaction mixture was partitioned between methylene chloride and water. The residue, 1.0 g, was recrystallized from chloroform–hexane, and gave α-fluorimino-4-chlorophenylacetamide, 0.10 g: mp 118–120; ^{19}F nmr, ϕ −24.4 in dimethylformamide solution.

Anal. Calcd for $C_8H_6ClFN_2O$: C, 47.9; H, 3.02; N, 13.96; F, 9.5. Found: C, 47.7; H, 3.15; N, 14.60; F, 10.1.

The filtrates were concentrated and crystallized from hexane to 0.82 g give methyl 4-chlorophenylacetate, mp 34–36°.

Preparation of Ethyl α-Fluorimino-4-chlorophenylacetate.—From 0.46 g of **1b** in 5 ml of ethanol, treated first with 2 drops of 4.3 *N* aqueous sodium hydroxide solution at −10°, followed by the usual acid hydrolysis, was obtained 0.03 g of α-fluorimino-4-chlorophenylacetamide, and 0.40 g of ethyl α-fluorimino-4-chlorophenylacetate, mp 35–37°.

Reaction of Methyl α-Fluoriminophenylacetate (3c) and Sodium Methoxide.—To 0.090 g of **3a** in 3 ml of methanol was added 0.60 ml of 1.30 *N* sodium methoxide in methanol. The mixture was heated at reflux for 1 hr, then cooled, and partitioned between methylene chloride and water. The methylene chloride solution was evaporated at reduced pressure; only benzonitrile (infrared spectrum and vpc) remained.

Beckmann Rearrangement of α-Fluorimino Esters.—The general procedure, used for the three esters cited below, is as follows. To 2.5 ml of sulfuric acid at 20° was added 0.40 g of the fluorimino ester. After 15 min at ambient temperature, the mixture was poured over ice, and the organic product was extracted into methylene chloride. The residue obtained upon evaporation of the methylene chloride was recrystallized from hexane–chloroform.

In this way methyl α-fluoriminophenyl acetate gave methyl oxanilide, mp 111–112.5° (lit.[10] mp 111°), the corresponding ethyl ester gave ethyl oxanilide, mp 64–65.5° (lit.[11] mp 66–67°), and ethyl α-fluorimino-4-chlorophenylacetate gave ethyl 4-chlorooxanilide, mp 159–160° (lit.[12] mp 155°). All three oxanilides gave acceptable elemental analyses.

Reaction of 4-Chlorophenylfluoriminonitrile (1b) and the Phenyl Grignard Reagent.—The procedure used to obtain the results reported in Table III are illustrated by the following. To a solution of 1.82 g (10 mmol) of **1b** in 20 ml of tetrahydrofuran at ice bath temperature was added 7.0 ml of 3M Arapahoe phenyl magnesium bromide. The mixture was allowed to warm to 25° over 1 hr, then stirred at 35° for another hour. The mixture was poured over ice–hydrochloric acid, and the organic product was extracted into methylene chloride. A small amount of benzonitrile was detected in the residue obtained upon evaporation of the methylene chloride; on an SF-96 column at 140°, a small peak (10% of the peak area of 4-chlorobenzonitrile–**1b** combined peak) due to benzonitrile was observed. Chromatography on silica gel gave, following the biphenyl fraction, 0.42 g of a mixture of 4-chlorobenzonitrile and **1b**, and then N-phenylimino-4-chlorophenylacetonitrile, 0.43 g, a bright yellow solid, mp 103–105°; further characterization is reported in Table III.

Reaction of Phenylfluoriminonitrile (1a) and 2,4,6-Trimethylbenzonitrile Oxide (7).—A mixture of 2.40 g of **7** and 2.25 g of **1a** in 50 ml of ether was allowed to stand for 3 days. At the end of this time, only a very weak ϕ −53 peak due to **1a** could be detected in the ^{19}F nmr spectrum; the major ^{19}F resonance was at ϕ −42.6. The ether was removed at reduced pressure, and the solid residue was recrystallized from hexane to give 3-mesityl-5-(α-fluoriminotolyl)-1,2,4-oxadiazole, mp 52–53°.

Registry No.—**1c** (*syn*), 16717-37-6; **1c** (*anti*), 16717-38-7; **2a**, 16753-57-4; **2b**, 16753-58-5; **2c** (*syn*), 16753-59-6; **2c** (*anti*), 16753-60-9; **3a**, 16717-39-8; **3b**, 16717-40-1; **3c** (*syn*), 16717-41-2; **3c** (*anti*), 16717-42-3; **3** (R = C_6H_5, R′ = C_2H_5), 16717-43-4; **3** (R = 4-ClC_6H_4, R′ = C_2H_5), 16717-44-5; **5** (*syn*), 16717-45-6; **5** (*anti*), 16717-46-7; **8** (R = C_6H_5), 16717-47-8; **8** (R = 4-ClC_6H_4), 16753-61-0; **8** (R = *n*-C_4H_9O, *syn*), 16717-48-9; **8** (R = *n*-C_4H_9O, *anti*), 16717-49-0; **8** (R = *n*-C_4H_9), 16749-02-3; α-fluoriminophenylacetamide, 16717-50-3; α-fluorimino-4-chlorophenylacetamide, 16717-51-4; *n*-butylfluoriminonitrile, 16717-52-5.

(10) G. D. Landers, *J. Chem. Soc.*, **85**, 984 (1904).
(11) H. Klinger, *Ann.*, **184**, 261 (1877).
(12) F. D. Chattaway and W. H. Lewis, *J. Chem. Soc.*, **89**, 155 (1906).