12d, 88425-61-0; 12e, 88425-62-1; 13, 88425-65-4; 14a, 88425-66-5; 14b, 88425-70-1; α-15, 88425-67-6; β-15, 88425-68-7; phenyl(bromodichloromethyl)mercury, 3294-58-4; phenyl(tribromomethyl)mercury, 3294-60-8.

Supplementary Material Available: A table listing all the bond angles from the crystallographic study of compound 12a (1 page). Ordering information is given on any current masthead page.

Trifluoroacetonitrile Oxide

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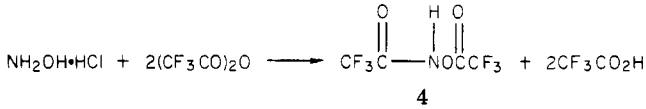
Trifluoroacetonitrile oxide (1) is a reactive intermediate that can be generated by the dehydrochlorination of trifluoroacetohydroximoyl chloride (2) with base. It reacts with mercaptans and amines in a stereospecific manner to give *Z* oximes 3 and 15 and forms a cycloadduct (10) with benzonitrile. In the absence of trapping agents, it dimerizes to give either the expected furoxan dimer 7 or the unusual dioxadiazine dimer 8, depending upon conditions. A convenient synthesis for 2 based on hydroxylamine hydrochloride, trifluoroacetic anhydride, and PCl_5 was developed to make 1 easily accessible.

Del'tsova, Ananyan, and Gambaryan[2] reported that trifluoroacetonitrile oxide (1) can be generated as a reactive intermediate by the dehydrochlorination of trifluoroacetohydroximoyl chloride (2) with triethylamine and trapped with electron-rich dipolariphiles such as vinyl ethers and vinyl amines. These investigators also report that in marked contrast to all other known nitrile oxides, 1 did not form a dimer.

We wished to investigate the reactions of thiols with 1 as a possible route to *N*-hydroxythioimidates 3, which are intermediates we needed to prepare fluorinated analogues of the insecticide methomyl.[3] However, the only literature methods for the preparation of the intermediate 2 are the reaction of capriciously explosive trifluorodiazoethane with nitrosyl chloride[4] and the low yield reaction of 1-nitro-2,2,2-trifluoroethane with benzoyl chloride and triethylamine.[5] Neither method is amenable to large-scale preparation.

In order to make the intermediate 2 more readily available, we developed a convenient, inexpensive method for its preparation. First, hydroxylamine hydrochloride was stirred at room temperature with 2 equiv of trifluoroacetic anhydride to give a nearly quantitative yield



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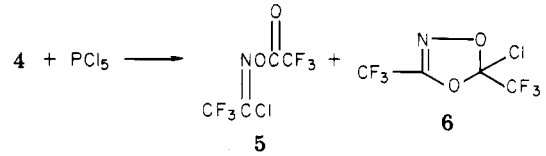
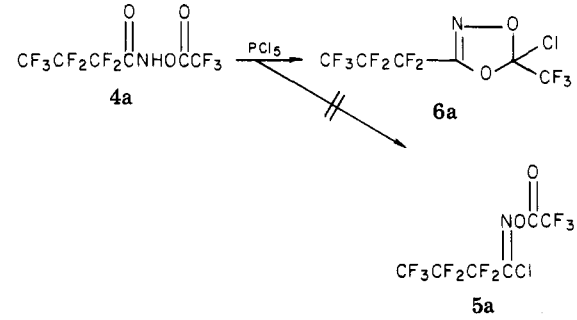


5 6

2

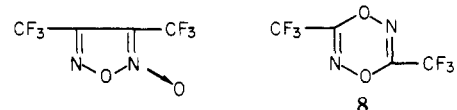
of *O,N*-bis(trifluoroacetyl)hydroxylamine[5] (4). Second, 4, in the form of a dry powder, was mixed with phosphorus pentachloride, and the resulting mixture was distilled to give the (trifluoroacetyl)hydroximoyl chloride 5 along with smaller amounts of the isomeric dioxazole 6. Mixing 5 with an equivalent amount of methanol gave 2 in 91% yield. Since none of these reactions required solvent, large-scale (2 mol or more) laboratory preparations of 2 were possible.

An attempt to prepare perfluorobutyrohydroximoyl chloride (2a) by a similar procedure was not successful. When *O*-(trifluoroacetyl)-*N*-(perfluorobutyryl)hydroxylamine (4a) was treated with PCl_5, only the dioxazole 6a was formed, to the exclusion of the hydroximoyl chloride 5a.



4a 6a 5a

Contrary to the previous report,[2] we found that trifluoroacetonitrile oxide (1), when generated from 2 by treatment with triethylamine in ether, gives a dimer if no trapping agent is present. The same dimer was also formed, along with some polymeric material, when other bases (NaH, CsF) and other solvents were utilized. This dimer has the dioxadiazine structure 8 and is probably



7 8

formed by the reaction of 2 or its anion with 1. A different dimer, having the furoxan structure 7, was formed when 1 was generated in the absence of excess 2 by a vapor-phase dechlorination of 2 over Ascarite (NaOH on asbestos). Both the dioxadiazine[6] and the furoxan[7] dimers of other

(1) Contribution Number 3301.
(2) Del'tsova, D. P.; Ananyan, E. S.; Gambaryan, N. B. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1971**, 362.
(3) Middleton, W. J. U.S. Patent 4 323 757, 1982.
(4) Kissinger, L. W.; McQuiston, W. E.; Schwartz, M. *Tetrahedron* **1963**, *19*, Suppl. 1, 137.
(5) Krzhizhevskii, A. M.; Mirzabekyants, N.S.; Cheburkov, Yu. A.; Knunyant, I. L. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1974**, 2513.
(6) (a) Brandi, A.; De Sarlo, F; Guara, A. *J. Chem. Soc., Perkin Trans. 1*, **1976**, 1827. (b) De Sarlo, F. *Ibid.* **1974**, 1951.

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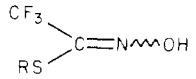
Table I. *N*-Hydroxythioacetimidates

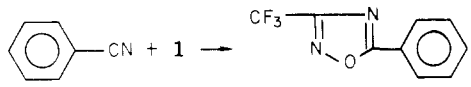


R	structure formula	config	mp, °C [bp, mm]	yield, %	anal.[a]	^{19}F NMR, δ
CH_3	$C_3H_4F_3NOS$	*Z*	52-54 [124-125]	83	C, H, F, N, S	−66.6 (q, *J* = 1 Hz)
CH_3	$C_3H_4F_3NOS$	*E*	60-62 [112-113]	74[b]	C, H, F, N, S	−66.2 (s)
CH_3CH_2	$C_4H_6F_3NOS$	*Z*	29-30	78	C, H, F, N	−66.0
CH_3CH_2	$C_4H_6F_3NOS$	*E*	28-30 [64 (4)]	50	C, H, N	−66.1
$CH_3CH_2CH_2$	$C_5H_8F_3NOS$	*Z*	[61 (1.4)]	86	C, H, F, N, S	−65.7
$(CH_3)_2CH$	$C_5H_8F_3NOS$	*Z*	[51-52 (2.0)]	64	C, H, F, N	−67.3
phenyl	$C_8H_6F_3NOS$	*Z*	74		C, H, N	−63.9
CH_2=$CHCH_2$	$C_5H_6F_3NOS$	*Z*	[62-68 (1.0)]	78	C, H, N	−66.5
n-butyl	$C_6H_{10}F_3NOS$	*Z*	42-44	78	C, H, F, N	−65.7
tert-butyl	$C_6H_{10}F_3NOS$	*Z*	[55 (1.7)]	81	C, H, F, N, S	−67.6
furfuryl	$C_7H_6F_3NO_2S$	*Z*	44-46	50	C, H, N	−66.5
benzyl	$C_9H_8F_3NOS$	*Z*	67-69	84	C, H, N	−66.1
CF_3	C_3HF_6NOS	*c*	[108-110]	31	C, H, F, N	−36.4, −68.1

[a] Analyses were within 0.4% of calculated values. [b] In mixture with 2.5% of the *Z* isomer. [c] Isomer configuration unknown.

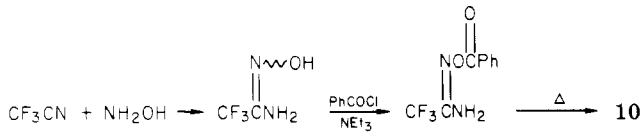
nitrile oxides have been reported previously.

Perfluorobutyronitrile does not react with **1**,[2] but nitriles more susceptible to electrophilic attack will form adducts. For example, **1** reacts with benzonitrile to form the oxadiazole adduct **10**. The structure of **10** was verified by

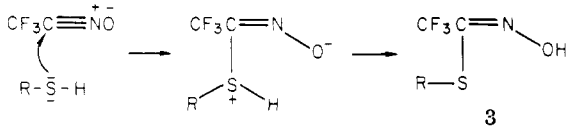


10

an independent synthesis from trifluoroacetonitrile.



Trifluoroacetonitrile oxide (**1**) adds to thiols to give the expected *N*-hydroxythioacetimidates **3**. The reaction



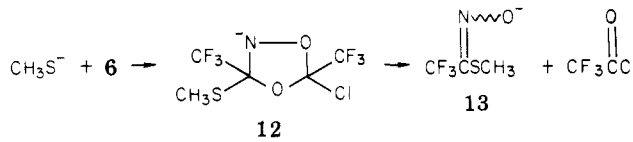
3

could be accomplished either by adding triethylamine to a solution in ether containing **2** and the thiol or more conveniently by adding **2** dropwise to a solution of the sodium salt of the thiol in methanol. The reaction is believed to proceed by the addition of the thiol to **1**, and not by direct reaction of **2** with the thiol anion, because of the stereochemistry involved. Only the *Z* isomers of the thioimidates **3** are formed, as verified by X-ray crystallography. This result is consistent with those observed by other investigators who examined the addition of thiols and other nucleophiles to nitrile oxides.[8]

Several *N*-hydroxy thioimidates **3** were prepared, both from aliphatic and aromatic thiols, and are listed in Table I. In every case, only the *Z* isomer was obtained when the reaction was carried out in the manner described.

The *E* isomers can be prepared by utilizing a process not involving the intermediacy of **1**. Thiol anions react with the byproduct dioxazole **6** to give predominately the *E* isomer of the *N*-hydroxythioacetamidates. This stereoselectivity toward the *E* isomer becomes even more pronounced at lower temperatures. For example, sodium methylmercaptide reacts with **6** at 0 °C to give a mixture containing 72% *E* isomer and 22% *Z* isomer, but at −70 °C a mixture containing 97% *E* isomer and only 3% *Z* isomer is obtained. Sublimation gave the *E* isomer of better than 99% isomeric purity.

The reason for the marked preference for the formation of the *E* isomer is unknown. The logical mechanism for its formation would be addition of the mercaptide anion to the C=N double bond of **6** to give the intermediate **12**,

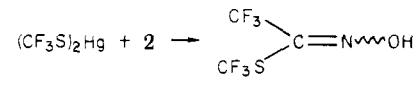


12 **13**

which could then decompose by elimination of trifluoroacetyl chloride to give the thioimidate anion **13**.

The two isomers can be equilibrated thermally by heating at 100 °C for 48 h to give a mixture containing more than 99% *Z* isomer and only a trace of the *E* isomer. The *Z* isomer appears to be more thermodynamically stable. The two isomers were also equilibrated photolytically to give a photostationary state containing 27% *E* isomer and 73% *Z* isomer.

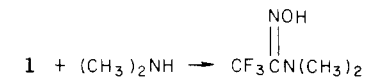
S-Trifluoromethyl 2,2,2-trifluoro-*N*-hydroxythioacetimidate (**14**) was prepared by reaction of **2** with $Hg(SCF_3)_2$.



14

Although only one isomer was formed, it is not known whether it is in the *E* or *Z* configuration or if **1** is an intermediate.

Dimethylamine also reacts very efficiently with **1** to give *N*,*N*-dimethyl-2,2,2-trifluoroacetohydroximamide (**15**).



15

Experimental Section

Fluorine NMR spectra were obtained on a Varian XL-100 instrument operated at 94.1 MHz with $CFCl_3$ as an internal

(7) Grundmann, C., *Fortschr. Chem. Forsch.* **1966**, *7*, 62.
(8) (a) Zinner, G.; Gunther, H. *Angew. Chem.* **1964**, *76*, 440. (b) Dignam, K. J.; Hegarty, A. F.; Quain, P. L. *J. Org. Chem.* **1978**, *43*, 388.

standard. Downfield shifts are reported as positive values.

***N,O*-Bis(trifluoroacetyl)hydroxylamine (4).** A 928-g (4.4 mol) sample of trifluoroacetic anhydride was added dropwise to 140 g (2 mol) of powdered hydroxylamine hydrochloride at such a rate that the evolution of hydrogen chloride did not become too vigorous. A reflux condenser cooled to −78 °C with solid carbon dioxide–acetone was used to prevent the evolved HCl from carrying out unreacted trifluoroacetic anhydride. The reaction mixture was stirred overnight and then evaporated to dryness under reduced pressure. The white residue was broken up and dried in a vacuum desiccator over P_2O_5 to give 373.73 g (83%) of crude **4**. A similar sample recrystallized from methylene chloride was obtained as colorless crystals: mp 40–50 °C; IR (Nujol) 1848 and 1706 cm^{-1}; ^{19}F NMR (ether) δ −73.7 (s) and −74.5 (s). Anal. Calcd for $C_4HF_6NO_3$: C, 21.35; H, 0.44; F, 50.56; N, 6.22. Found: C, 21.38; H, 0.87; F, 50.81; N, 6.76.

2,2,2-Trifluoro-*O*-(trifluoroacetyl)acetohydroximoyl Chloride (5) and 2-Chloro-2,5-bis(trifluoromethyl)-1,3,4-dioxazole (6). A mixture of 433 g (1.92 mol) of crude *N,O*-bis(trifluoroacetyl)hydroxylamine and 433 g (2.08 mL) of phosphorus pentachloride was gently heated under a reflux condenser cooled to −78 °C with solid carbon dioxide–acetone until the mixture liquified and evolution of HCl ceased. Distillation gave 49.28 g (11%) of **6** as a colorless liquid [bp 52–53 °C; n^{25}_D 1.3000; IR (liquid) 1661 cm^{-1} (C=N); ^{19}F NMR (CCl_3F) δ −68.0 (s, 3 F) and −82.4 (s, 3 F)] and 271.51 g (58%) of **5** as a colorless liquid [bp 83–84 °C; n^{25}_D 1.3272; IR (liquid) 1634 (C=N) and 1848 cm^{-1} (C=O); ^{19}F NMR (CCl_3F) δ −70.0 (s, 3 F) and −74.1 (s, 3 F)]. Anal. Calcd for $C_4ClF_6NO_2$: C, 19.73; Cl, 14.56; F, 46.82; N, 5.75. Found (**6**): C, 19.95; Cl, 14.07; F, 46.57; N, 5.68. Found (**5**): C, 19.50; Cl, 14.87; F, 46.68; N, 5.87.

Trifluoroacetohydroximoyl Chloride (2). Methanol, 21.0 g (0.65 mol) was added dropwise to 153 g (0.63 mol) of **5** cooled to 0 °C. The reaction mixture was allowed to warm to 25 °C and then distilled to give methyl trifluoroacetate, bp 44 °C, and then 84.8 g (91%) of **2** as a colorless liquid: bp 90–91 °C; IR (liquid) 1637 cm^{-1} (C=N); ^{19}F NMR ($CFCl_3$) δ −70.1 (s). Anal. Calcd for C_2HClF_3NO: C, 16.28; H, 0.69; Cl, 24.04; F, 38.64; N, 9.50. Found: C, 16.38; H, 0.98; Cl, 24.18; F, 38.77; N, 9.51.

3,6-Bis(trifluoromethyl)-1,4,2,5-dioxadiazine (8). A 14.75-g (0.1 mol) sample of **2** was added dropwise to a suspension of 30.4 g (0.2 mol) of cesium fluoride in 100 mL of diglyme. The undissolved solid was filtered off, and the filtrate was distilled to give 3.7 g (34%) of **8**: bp 62–63 °C; IR (liquid) 1684 and 1645 cm^{-1}; ^{19}F NMR (CCl_3F) δ −72.1 (s). Anal. Calcd for $C_4F_6N_2O_2$: C, 21.63; F, 51.34; N, 12.62. Found: C, 21.63; F, 51.21; N, 12.62.

The pot residue was mixed with water, and the oil that precipitated was washed thoroughly with water and then dried in a vacuum desiccator to give 2.0 mL of viscous liquid. Analysis indicates this liquid is a low polymer of CF_3CNO: ^{19}F NMR (CCl_3) δ −72.2 (br, $w_{1/2}$ 20 Hz). Anal. Calcd for $(C_2F_3NO)_n$: C, 21.63; F, 51.34; N, 12.62. Found: C, 20.32; F, 50.81; N, 12.50.

3,4-Bis(trifluoromethyl)furoxan[4] (7). A stream of nitrogen was bubbled through a 25-g sample (0.17 mol) of **2**, and the entrained vapors were passed through a column containing 200 g of Ascarite (NaOH on asbestos) and then condensed in a cold trap (−78 °C). The Ascarite gained 14.3 g. The condensate in the trap (6.8 g, 98% pure by GC) was distilled to give 5.7 g (30%) of **7** as a colorless liquid: bp 88 °C; n^{25}_D 1.3471; ^{19}F NMR (CCl_3F) δ −62.7 (q, J = 6 Hz, 3 F) and −65.1 (q, J = 6 Hz) with no coalescence at 190 °C. Anal. Calcd for $C_4F_6N_2O_2$: C, 21.64; F, 51.34; N, 12.62. Found: C, 21.76; F, 51.12; N, 12.43.

Reaction of Benzonitrile with 1. A solution of 2.52 g (0.025 mol) of triethylamine in 10 mL of ether was added dropwise to a stirred solution of 3.69 g (0.025 mol) of **2** and 2.58 g (0.025 mol) of benzonitrile in 25 mL of ether. The reaction temperature was maintained at 25–30 °C by cooling. The precipitated triethylamine hydrochloride was filtered off, and the filtrate was distilled to give 1.79 g (70% recovered) of benzonitrile and 0.67 g (13%) of 5-phenyl-3-(trifluoromethyl)-1,2,4-oxadiazole (**10**) as a colorless liquid, bp 210–212 °C. This sample was identical by IR and GC with the oxadiazole prepared from *O*-benzoyl-2,2,2-trifluoroacetohydroximamide.

When the same dehydrochlorination reaction was run with triethylamine without benzonitrile present, **8** and the polymer of CF_3CNO were obtained.

2,2,2-Trifluoroacetamide *O*-Benzoyloxime. Benzoyl chloride, 126.5 g (0.9 mol), was added dropwise to a solution of 113.6 g (0.89 mol) of trifluoroacetohydroximamide and 91 g (0.9 mol) of triethylamine in 800 mL of ether cooled in an ice bath. The solid that precipitated was collected on a filter and washed with ether. The filtrate and ether wash were evaporated to dryness, and the residual solid was recrystallized from benzene to give 28.7 g of the benzoyl derivative. The solid precipitate was washed with water to remove the triethylamine hydrochloride, and the residue was recrystallized from benzene to give an additional 110.2 g of the benzoyl derivative. The total yield was 138.9 g (73%) of colorless crystals: mp 151–152 °C; ^{19}F NMR (Me_2SO-d_6) δ −69.1 (s); IR (KBr) 1742 cm^{-1} (C=O) and 1661 cm^{-1} (C=N). Anal. Calcd for $C_9H_7F_3N_2O_2$: C, 46.56; H, 3.04; F, 24.55; N, 12.07. Found: C, 46.70; H, 3.00: F, 24.60; N, 11.96.

2,2,2-Trifluoroacetamide Oxime. A solution of 1 mol of sodium methoxide (prepared from 23 g of sodium) in 600 mL of methanol was added dropwise to a stirred suspension of 69.5 g (1 mol) of hydroxylamine hydrochloride in 200 mL of methanol. The solution was filtered to remove the sodium chloride and then cooled to 0 °C. Trifluoroacetonitrile, 95 g (1 mol) was then distilled into the cooled solution. The methanol was evaporated under reduced pressure at room temperature. The residual oil (114 g, 89%) solidified on standing overnight. The resulting solid was recrystallized from Freon 113 to give 85 g (66%) of the amidoxime as colorless, very hydroscopic crystals: mp 36–38 °C; IR (KBr) 1698 cm^{-1}; ^1H NMR (CD_3CN) δ 8.51 (s, 1 H) and 5.25 (br, 2 H); ^{19}F NMR (CD_3CN) δ −70.5 (s). Anal. Calcd for $C_2H_3F_3N_2O$: C, 18.76; H, 2.36; F, 44.51; N, 21.88. Found: C, 19.05; H, 2.39; F, 44.66; N, 21.90.

When exposed to moist air, this amidoxime first liquifies and then resolidifies to give a nonhygroscopic hemihydrate, mp 39–40 °C. Anal. Calcd for $C_2H_3F_3N_2O \cdot {}^1/_2H_2O$: C, 17.52; H, 2.94; F, 41.59; N, 20.44. Found: C, 17.36; H, 3.39; F, 41.39; N, 20.18.

5-Phenyl-3-(trifluoromethyl)-1,2,4-oxadiazole (10). A 117-g (0.5 mol) sample of 2,2,2-trifluoroacetamide *O*-benzyloxime was melted and then heated strongly in a simple still. A liquid distilled between 100–200 °C. The water layer (9 mL) was removed from the distillate, and the distillate was dried ($MgSO_4$) and redistilled to give 99.8 g (94%) of **10** as a colorless liquid: bp 212 °C; mp 15–16 °C; n^{25}_D 1.4811; ^{19}F NMR (CCl_3F) δ −66.7 (s). Anal. Calcd for $C_9H_5F_3N_2O$: C, 50.48; H, 2.35; F, 26.87; N, 13.08. Found: C, 50.71; H, 2.92; F, 26.87; N, 13.08.

***S*-Methyl (*Z*)-2,2,2-Trifluoro-*N*-hydroxythioacetimidate (Table I).** Methanethiol, 38 mL (measured at 0 °C, 0.68 mol) was distilled into a solution prepared by dissolving 14.7 g (0.638 mol) of sodium in 260 mL of methanol. The resulting solution was cooled to 0 °C, and 94.1 g (0.638 mol) of trifluoroacetohydroximoyl chloride was added dropwise, keeping the temperature below 10 °C. The reaction mixture was stirred at room temperature overnight, filtered to remove NaCl, and evaporated to dryness under reduced pressure. (Care should be taken to avoid loss of product because of sublimation.) The residue was sublimed at 50–60 °C and 0.5-mm pressure to give 84.71 g (83%) of *S*-methyl (*Z*)-2,2,2-trifluoro-*N*-hydroxythioacetimidate as large, colorless crystals: mp 52–54 °C; IR (KBr) 3279 (OH) and 1608 cm^{-1} (C=N); ^1H NMR ($CDCl_3$) δ 2.53 (m, 3 H) and 8.07 (s, 1 H). An X-ray crystal structure analysis showed the compound to have a *Z* configuration, with the S and O atoms cis to one another.[9]

The other thioimidates having the *Z* configuration listed in Table I were prepared in a similar manner, substituting other thiols for methanethiol.

***S*-Methyl (*E*)-2,2,2-Trifluoro-*N*-hydroxythioacetimidate.** Methanethiol, 28 mL (0.56 mol), was distilled into a solution prepared by dissolving 9.2 g (0.4 mol) of sodium in 300 mL of methanol. The reaction mixture was cooled to −70 °C, and 97.4 g (0.4 mol) of **6** was added dropwise, keeping the temperature at −70 to −75 °C. The reaction mixture was warmed to room temperature, stirred for 18 h, and then filtered. The filtrate was evaporated to dryness, and the residue was sublimed at 50 °C and 5-mm pressure. The first fraction, 5.21 g, was 78% *E* isomer and 28% *Z* isomer by ^{19}F NMR. The second fraction, 43.71 g

(9) Harlow, R., unpublished results.

(69%), was 99% *E* isomer by ^{19}F NMR, mp 60–62 °C. (Total yield of both isomers, 77%.)

The reaction was considerably less selective when run at 0 °C giving 72% *E* isomer [bp 112–113 °C (200 mm)] and 28% *Z* isomer [bp 124–125 °C (200 mm)] in 57% yield.

Photostationary State of *E* and *Z* Isomers of *S*-Methyl 2,2,2-Trifluoro-*N*-hydroxythioacetimidate. A 6% solution of *S*-methyl (*E*)-2,2,2-trifluoro-*N*-hydroxythioacetimidate in $CDCl_3$ was irradiated with a Hanovia 450-W medium-pressure mercury arc lamp through a water-cooled quartz filter. After 20 min of irradiation, a photostationary state consisting of 27% *E* isomer and 73% *Z* isomer was reached (analysis by ^{19}F NMR). A 6% solution of the pure *Z* isomer was irradiated under the same conditions and reached the same photostationary state in 2 h. *Z* Isomer: $\lambda_{max}^{CH_2Cl_2}$ = 242 nm (*E* 5100). *E* Isomer: $\lambda_{max}^{CH_2Cl_2}$ = 252 nm (ε 7530).

***S*-Ethyl (*E*)-2,2,2-Trifluoro-*N*-hydroxythioacetimidate.** Ethanethiol, 17 mL (0.23 mol), was added dropwise to a solution prepared by dissolving 4.14 g (0.18 mol) of sodium in 150 mL of methanol. The reaction mixture was cooled to −70 °C, and 43.83 g (0.18 mol) of **6** was added dropwise. The reaction mixture was stirred at ambient temperature for 3 days, filtered to remove precipitated sodium chloride, and evaporated to dryness under reduced pressure. The residue was sublimed at 50 °C (1-mm pressure), and the sublimate was condensed in a cold (−78 °C) receiver and then pressed between layers of filter paper to give 15.7 g (50%) of colorless crystals: mp 28–30 °C; ^1H NMR ($CDCl_3$) δ 1.33 (t, *J* = 7 Hz, 3 H), 2.89 (q, *J* = 7 Hz, 2 H), 8.64 (OH).

The UV spectrum of this *E* isomer gave $\lambda_{max}^{CH_2Cl_2}$ 2550 Å (ε 7310), as contracted to the corresponding *Z* isomer, which gave $\lambda_{max}^{CH_2Cl_2}$ 2430 Å (ε 3320).

***N*,*N*-Dimethyl-2,2,2-trifluoroacetohydroximamide (15).** A solution of 29.5 g (0.2 mol) of **2** in 30 mL of ether was added dropwise to a solution of 22.5 g (0.5 mol, 33 mL at 0 °C) of dimethylamine in 300 mL of ether cooled to −70 °C. The reaction mixture was allowed to warm to 25 °C stirred 18 h, and then filtered to remove the precipitated dimethylamine hydrochloride. The filtrate was distilled to give 26.74 g (86%) of **15** as a colorless liquid: bp 66–67 °C (10 mm); ^{19}F NMR ($CDCl_3$) δ −65.8 (s); ^1H NMR ($CDCl_3$) δ 3.03 (s). Anal. Calcd for $C_4H_7F_3N_2O$: C, 30.77; H, 4.52; F, 36.51; N, 17.95. Found: C, 31.21; H, 4.85; F, 36.53; N, 18.15.

***N*-(Perfluorobutyryl)-*O*-(trifluoroacetyl)hydroxylamine (4a).** Trifluoroacetic anhydride, 54.6 g (0.26 mol), was added dropwise to a 57.3-g (0.25 mol) sample of perfluorobutyrohydroxamic acid.[10] The reaction mixture became warm and liquified. The trifluoroacetic acid that formed and the excess trifluoroacetic anhydride were distilled off at reduced pressure (1 mm at 25 °C), and the solid residue was recrystallized from methylene chloride under nitrogen to give 57.07 g (70%) of **4a** as colorless crystals: mp 39–41 °C; ^{19}F NMR (CD_3CN) δ −73.5 (s, 3 F), −80.8 (t, *J* = 9 Hz, 3 F), −120.5 (q, *J* = 9 Hz, 2 F), −127.1 (s, 2 F). Anal. Calcd for $C_6HF_{10}NO_3$: C, 22.17; H, 0.31; F, 58.45; N, 4.31. Found: C, 22.20; H, 0.67; F, 58.28; N, 4.37.

2-Chloro-2-(trifluoromethyl)-5-(perfluoropropyl)-1,3,4-dioxazole (6a). A mixture of 49.25 g (0.15 mol) of **4a** and 41.66 g (0.2 mol) of phosphorus pentachloride was heated until the reaction mixture liquified and evolution of HCl ceased. Distillation gave 18.35 g (28%) of **6a** as a colorless liquid, bp 85–92 °C, contaminated with some $POCl_3$. An analytical sample was prepared by washing with water, drying (Al_2O_3), and redistilling to give a purified sample: bp 90–91 °C; n_D^{25} 1.3036; IR (liquid) 1647 cm^{-1} (C=N); ^{19}F NMR (CCl_3F) δ −81.0 (t, *J* = 9 Hz, 3 F), −82.4 (s, 3 F), −116.1 (m, 2 F), −127.0 (s, 2 F). Anal. Calcd for $C_6ClF_{10}NO_2$: C, 20.98; Cl, 10.32; F, 55.31; N, 4.08. Found: C, 21.17; Cl, 10.36; F, 55.24; N, 4.74.

***S*-Trifluoromethyl 2,2,2-Trifluoro-*N*-hydroxythioacetimidate (14).** A mixture of 40.28 g (0.1 mol) of mercury trifluoromethylmercaptide[11] and 14.7 g (0.1 mol) of **2** was heated at reflux for 18 h. The volatile portion of the reaction mixture was distilled under reduced pressure into a cold trap (−78 °C) and then redistilled to give 6.55 g (31%) of **14** as a colorless liquid: bp 108–110 °C; IR (liquid) 3546, 3367 (OH), 1605 cm^{-1} (C=N); ^{19}F NMR (CCl_3F) δ −36.4 (q, *J* = 4.2 Hz, 3 F) and −68.1 (q, *J* = 4.2 Hz, 3 F); ^1H NMR (CCl_3F) δ 9.70 (s).

Registry No. 1, 32990-21-9; **2**, 815-03-2; (*Z*)-**3** (R = CH_3), 82985-93-1; (*E*)-**3** (R = CH_3), 82985-94-2; (*Z*)-**3** (R = CH_3CH_2), 82985-97-5; (*E*)-**3** (R = CH_3CH_2), 88326-75-4; (*Z*)-**3** (R = $CH_3CH_2CH_2$), 82986-00-3; (*Z*)-**3** (R = $(CH_3)_2CH$), 82985-99-7; (*Z*)-**3** (R = phenyl), 82986-02-5; (*Z*)-**3** (R = CH_2=$CHCH_2$), 82986-03-6; (*Z*)-**3** (R = *n*-butyl), 88326-76-5; (*Z*)-**3** (R = *tert*-butyl), 82986-01-4; (*Z*)-**3** (R = furfuryl), 88326-77-6; (*Z*)-**3** (R = benzyl), 88326-78-7; **4**, 684-78-6; **4a**, 88326-80-1; **5**, 82817-12-7; **6**, 82985-92-0; **6a**, 88326-81-2; **7**, 707-71-1; **8**, 88326-82-3; **10**, 86657-10-5; **14**, 88326-79-8; **15**, 88326-83-4; $(CF_3CO)_2O$, 407-25-0; $NH_2OH{\cdot}HCl$, 5470-11-1; $CF_3CO_2CH_3$, 431-47-0; CF_3CN, 353-85-5; $(CH_3)_2NH$, 124-40-3; $(CF_3S)_2Hg$, 21259-75-6; benzonitrile, 100-47-0; 2,2,2-trifluoroacetamide *O*-benzoyloxime, 88326-84-5; benzoyl chloride, 98-88-4; trifluoroacetohydroximamide, 4314-35-6; perfluorobutyrohydroxamic acid, 87050-96-2; methanethiol, 74-93-1; ethanethiol, 75-08-1; 1-propanethiol, 107-03-9; 2-propanethiol, 75-33-2; benzenethiol, 108-98-5; allyl mercaptan, 870-23-5; *n*-butyl mercaptan, 109-79-5; *tert*-butyl mercaptan, 75-66-1; furfuryl mercaptan, 98-02-2; benzyl mercaptan, 100-53-8; trifluoromethanethiol, 1493-15-8.

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Notes

Active Esters of Polymer-Bound 4-Hydroxy-3-nitrobenzophenone as Useful Acylating Reagents. Application to Peptide Synthesis

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Polymeric active esters have found considerable use as acylating reagents in peptide synthesis,[1,2] preparation of semisynthetic penicillins and cephalosporins,[3] studying intrapolymer interactions,[4] and in multipolymer reactions with carbanions.[5] They are easily separated from low molecular weight reactants by filtration or selective pre-

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