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SOME NOVEL OXIME ETHERS. THE SYNTHESIS OF 1,1-DIFLUORO-2-ALKOXYMETHANIMINES

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SUMMARY

The syntheses of four novel 1,1-difluoro-2-alkoxymethanimines, $\text{RON}=\text{CF}_2$, are reported. The oxime ethers are prepared in excellent yield by dehydrofluorination of the amines, $\text{RON}(\text{H})\text{CF}_3$ ($\text{R}=\text{CF}_3, (\text{CF}_3)_2\text{CF}, \text{CH}_3, (\text{CH}_3)_3\text{C}$) with KF . These oxime ethers are thermally stable at 24°C and are characterized by IR, NMR, and physical properties. The two perfluoro compounds undergo dimerization to give $\text{CF}_3\text{N}(\text{OR})\text{CF}=\text{NOR}$ in the presence of CsF at room temperature.

INTRODUCTION

The chemistry of a unique group of compounds represented by the formula $\text{RO}=\text{N}=\text{CR}^1\text{R}^2$ is relatively unknown in the literature. The commonly, though infrequently, reported examples of oxime ethers are generally limited to structures where R^1 and R^2 are alkyls or aryls. Surprisingly, simple analogues such as $\text{RON}=\text{CH}_2$ and $\text{RON}=\text{CF}_2$ have not been synthesized.

Recent studies of the chemistry of the novel oxaziridine, $\text{CF}_3\overline{\text{NCF}_2\text{O}}$,¹ in our laboratory have led to the syntheses of a number of alkoxyamines, $\text{CF}_3\text{N}(\text{OR})\text{H}$.² We now report the synthesis of four oxime ethers of the type $\text{RON}=\text{CF}_2$ from these alkoxyamines by dehydrofluorination.

EXPERIMENTAL

General. All volatile compounds were handled in glass and stainless steel vacuum systems as previously described.¹ Characterization of new compounds was carried out in the usual way. NMR chemical shifts are negative when found at higher fields than the reference and visa-versa. The amines, $\text{CF}_3\text{N}(\text{OR})\text{H}$, were prepared by the literature methods.²

Reactions of $\text{CF}_3\text{N}(\text{OR})\text{H}$ with KF . Reactions were carried out in 75mL stainless steel reactors fitted with a stainless steel valve. In a typical reaction, dried KF (5g) was placed in the reactor and pumped under vacuum. The vessel was then cooled to -195°C , evacuated, and the amine was added by vacuum transfer. The mixture was allowed to stand at room temperature for 14 hours. The products were separated by pumping through traps and held at various temperatures. Pure samples of the oxime ethers were obtained by GLC on 10' x 3/8" stainless steel column packed with 40% Halocarbon 11-21 polymer oil on Chromosorb P.

$\text{CF}_3\text{ON}=\text{CF}_2$: mp- 104.5°C ; bp- 16.4°C ; mol. wt. 149.0, calcd. 150.2; $\log P$ (torr) = $6.467-586.86/T - 857 \times 10^2/T^2$; $\Delta H_{\text{vap}} = 5.74$ kcal/mol; $\Delta S_{\text{vap}} = 22.4$ eu; IR 1795 (w), 1760 (s), 1438 (w), 1375 (s), 1280 (vs), 1230 (vs), 1180 (m), 1082 (vw), 1050 (s), 959 (vw), 897 (m), 730 (vw), 705 (m), 640 (w), 615 (w), 580 (w) cm^{-1} ; NMR $\text{CF}_3^{\text{M}}\text{ON}=\text{CF}^{\text{A,B}}$, $\phi_{\text{M}}^* - 67.7$, d-d; $\phi_{\text{A}}^* - 88.6$ br.d; $\phi_{\text{B}}^* - 57.5$ br.d; $J_{\text{AM}} = 3.2$ Hz, $J_{\text{BM}} = 1.5$ Hz, $J_{\text{AB}} = 58.5$ Hz.

$(\text{CF}_3)_2\text{CFON}=\text{CF}_2$: mp- 95° to -93.5°C ; bp 37.3°C ; mol. wt. 249.0, calcd. 250.06; $\log P$ (torr) = $4.699-334.83/T-2792 \times 10^2/T^2$; $\Delta H_{\text{vap}} = 6.70$ kcal/mol; $\Delta S_{\text{vap}} = 21.6$ eu; IR 1755 (s), 1375 (s), 1333 (m), 1317 (m), 1250 (vs), 1210 (w), 1170 (s), 1123 (s), 1032 (m), 1015 (s), 949 (vw), 920 (w), 795 (w), 740 (m), 718 (m), 643 (w), 555 (vw), 538 (w); NMR $(\text{CF}_3^{\text{M}})_2\text{CF}^{\text{N}}\text{ONCF}^{\text{A,B}}$, $\phi_{\text{M}}^* - 77.8$, d; $\phi_{\text{N}}^* - 138.7$, m; $\phi_{\text{A}}^* - 87.1$, br.d; $\phi_{\text{B}}^* - 56.6$, br.d; $J_{\text{MN}} = 2.0$ Hz, $J_{\text{AB}} = 60$ Hz, J_{NA} or $J_{\text{NB}} = 0.4$ Hz, J_{MA} or $J_{\text{MB}} = 0.8$ Hz.

$\text{CH}_3\text{ON}=\text{CF}_2$: mp- 79.4° to -78.7°C ; bp- 0.9°C ; mol. wt. 95.0, calcd. 94.85; $\log P$ (torr) = $6.557-693.39/T-837 \times 10^2/T^2$; $\Delta H_{\text{vap}} = 5.98$ kcal/mol; $\Delta S_{\text{vap}} = 22.0$ eu; IR 2960 (m), 2915 (w), 2830 (w), 1825 (w), 1740 (s), 1615 (w), 1480 (w), 1465 (w), 1345 (s), 1267 (w), 1243 (w), 1197 (m), 1085 (s), 1023 (vw), 995 (m), 924 (w), 733 (vw), 613 (w); NMR $\text{CH}_3^{\text{X}}\text{ONCF}^{\text{A,B}}$, $\delta_{\text{X}} 3.9$, d; $\phi_{\text{A}}^* - 92.6$, d; $\phi_{\text{B}}^* - 63.2$, d; $J_{\text{XF}} = 2.4$ Hz, $J_{\text{AB}} = 39$ Hz.

$(\text{CH}_3)_3\text{CON}=\text{CF}_2$: mp- 104.5°C ; bp 56.7°C ; mol. wt. 137.1, calcd. 137.06; $\log P$ (torr) = $7.886-1651/T$, $\Delta H_{\text{vap}} = 7.55$ kcal/mol; $\Delta S_{\text{vap}} = 22.9$ eu; IR 3000 (m), 2950 (w), 2900 (vw), 1785 (vw), 1750 (s), 1708 (vw), 1440 (w), 1395 (vw), 1373 (m), 1338 (s), 1260 (m), 1200 (m), 1172 (m), 1045 (s), 915 (vw), 890 (sh), 610 (w), 580 (vw); NMR $(\text{CH}_3^{\text{X}})_3\text{CONCF}^{\text{A,B}}$, $\delta_{\text{X}} 1.25$ s, $\phi_{\text{A}}^* - 93.2$, d; $\phi_{\text{B}}^* - 65.6$, br.d; $J_{\text{AB}} = 35$ Hz.

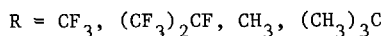
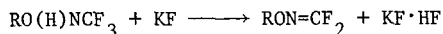
Reactions of $\text{RON}=\text{CF}_2$ ($\text{R}=\text{CF}_3$; $\text{CF}(\text{CF}_3)_2$) with CsF . Reactions were carried out in a 100 mL glass bulb fitted with a glass-Teflon valve. In a typical reaction, dried CsF ($\sim 0.5\text{g}$) was placed in the reactor and pumped under vacuum. The vessel was then cooled to -195°C and $\text{RON}=\text{CF}_2$ (2mmol) was added by vacuum transfer. The mixture was allowed to stand at room temperature overnight. The products were separated by pumping through traps at -70 , -110 , and -195°C . Both -110 and -195°C traps contained traces of unidentified material. Relatively pure dimer of $\text{RON}=\text{CF}_2$ ($\sim 1\text{mmol}$) was obtained by refractionation of the contents of the -70°C trap.

$\text{CF}_3\text{N}(\text{OCF}_3)\text{CF}=\text{NOCF}_3$: mp- 101.7°C ; mol. wt. 300.4, calcd. 302.1; IR 1710 (s), 1342 (s), 1290 (vs), 1235 (vs), 1195 (vs), 1095 (w), 1080 (vw), 1050 (m), 1018 (m), 987 (m), 972 (m), 920 (m), 898 (w), 840 (m), 758 (w), 740 (m), 700 (w), 662 (m), 655 (m), 625 (w), 600 (m), 558 (vw), 530 (vw); NMR $\text{CF}_3^{\text{A}}\text{N}(\text{OCF}_3^{\text{B}})\text{CF}^{\text{C}}=\text{NOCF}_3^{\text{D}}$, $\phi_{\text{A}}^* -68.9$, d-q; $\phi_{\text{B}}^* -66.5$, d-q; $\phi_{\text{C}}^* -62.8$, q-q; $\phi_{\text{D}}^* -66.4$, d; $J_{\text{AB}} = 4.0$ Hz, $J_{\text{BC}} = 5.5$ Hz, $J_{\text{CD}} = 1.8$ Hz.

$\text{CF}_3\text{N}[\text{OCF}(\text{CF}_3)_2]\text{CF}=\text{NOCF}(\text{CF}_3)_2$: mp- 81.3°C ; IR 1702 (s), 1325 (vs), 1284 (s), 1250 (vs), 1210 (s), 1193 (s), 1160 (s), 1115 (vs), 1058 (w), 1018 (s), 950 (w), 928 (m), 872 (w), 790 (w), 757 (w), 730 (s), 720 (m), 662 (m), 610 (w), 552 (w), 536 (w); NMR $\text{CF}_3^{\text{A}}\text{N}[\text{OCF}^{\text{B}}(\text{CF}_3^{\text{C}})_2]\text{CF}^{\text{D}}=\text{NOCF}^{\text{E}}(\text{CF}_3^{\text{C}})_2$, $\phi_{\text{A}}^* -69.0$, m; $\phi_{\text{B}}^* -78.0$ br; $\phi_{\text{C}}^* -77.9$ d; $\phi_{\text{D}}^* -60.8$, br; $\phi_{\text{E}}^* -138.4$, m; $J_{\text{AD}} = 8$ Hz, $J_{\text{AB}} = 8$ Hz, $J_{\text{AC}} = 1.6$ Hz, J_{BC} and $J_{\text{CE}} = 2$ Hz, $J_{\text{DE}} = 2$ Hz.

RESULTS AND DISCUSSION

The amines, $\text{CF}_3\text{N}(\text{OR})\text{H}$, readily lose HF in the presence of KF to give the corresponding oxime ethers, $\text{RON}=\text{CF}_2$, in high yield. These four oxime ethers



are of surprising stability. No decomposition of the compounds was evidenced at 24°C during handling in glass or stainless steel vacuum system. The characterization of these compounds by IR, NMR, and molecular weight is straightforward. The IR spectra exhibit a characteristic strong $\nu(\text{N}=\text{C})$ near 1750 cm^{-1} and strong $\nu(\text{CF}_2)$ antisymmetric and symmetric stretches in the region $1338\text{--}1375$ and $1015\text{--}1085\text{ cm}^{-1}$, respectively. These values are similar to those for $\text{CF}_2=\text{NCl}_3$ and $\text{CF}_2=\text{NF}_4$.

The two doublets seen in the NMR spectra for the methylene fluorines clearly demonstrate the nonequivalence of these two fluorines, which is due to the non-collinear conformation of the alkoxy group with the N=C double bond. The chemical shifts of the two geminal fluorines are strikingly different (Table I) and the very small values of J/Δ gives rise to simple first-order spectra. No attempt was made to determine which resonance is cis or trans to the alkoxy group. However, in $\text{CF}_2=\text{NF}$ and cis and trans $\text{CFCl}=\text{NF}$ the methylene fluorine trans to the NF fluorine on nitrogen is at much higher field than the cis fluorine.⁵ In all probability, similar considerations apply here.

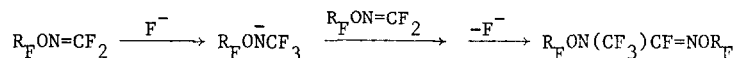
Table I. Chemical Shifts^a and Coupling Constants of the Methylene Fluorines in $\text{RON}=\text{CF}^{\text{A}}\text{F}^{\text{B}}$

R	ϕ_{A}	ϕ_{B}	J_{AB} (Hz)	J/Δ
CF_3	-88.6	-57.5	58.5	0.02
$(\text{CF}_3)_2\text{CF}$	-87.1	-56.6	60.0	0.02
CH_3	-92.6	-63.2	39.0	0.01
$(\text{CH}_3)_3\text{C}$	-93.2	-65.6	35.0	0.01

^a. Upfield from CFCl_3 as an internal standard.

The chemical shifts of the methylene fluorines also vary with respect to the alkoxy groups, decreasing as the electron withdrawing effect increases (Table I). We speculated that the perfluoro oxime ethers ($\text{R} = \text{CF}_3$; $(\text{CF}_3)_2\text{CF}$) are more susceptible to nucleophilic attack at carbon than the alkoxy ($\text{R} = \text{CH}_3$; $(\text{CH}_3)_3\text{C}$) analogues. Reactions of the oxime ethers with CsF indeed proved this to be the case. Both the perfluoro compounds dimerize in the presence of CsF whereas the other two compounds give no reaction under similar condition.

The CsF catalyzed dimerization of the perfluoro oxime ethers probably proceeds according to the following scheme.



The initial nucleophilic attack at carbon by fluoride ion would give an alkoxymethanamine ion, which would then attack another molecule of oxime ether to displace a fluoride ion and form the dimer. Similar dimerization has been observed for $\text{CF}_3\text{N}=\text{CF}_2$ ⁶ and $\text{CF}_2=\text{NF}$ ⁷.

The two dimers, $\text{CF}_3\text{N}(\text{OCF}_3)\text{CF}=\text{NOCF}_3$ and $\text{CF}_3\text{N}[\text{OCF}(\text{CF}_3)_2]\text{CF}=\text{NOCF}(\text{CF}_3)_2$, are also characterized by IR, NMR, and physical properties. It is interesting to note that, in the NMR spectrum of $\text{CF}_3\text{N}[\text{OCF}^{\text{A}}(\text{CF}_3)_2]\text{CF}=\text{NOCF}^{\text{B}}(\text{CF}_3)_2$, $\text{F}^{\text{A}}(\phi^* -78.0)$ is seen at much lower field than $\text{F}^{\text{B}}(\phi^* -138.4)$. This may be due to the greater steric hindrance of the $\text{OCF}^{\text{A}}(\text{CF}_3)_2$ group in the molecule, which may result from F^{A} being subjected to the shielding effect of the N=C bond.

The dehydrofluorination of amines of the type $\text{CF}_3\text{N}(\text{OR})\text{H}$ provides an excellent route to a number of oxime ethers of the type $\text{RON}=\text{CF}_2$. The examples in this paper have already shown some of the interesting chemistry of these novel imines. Further work on their chemistry is underway.

ACKNOWLEDGEMENT

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REFERENCES

- 1 E. R. Falardeau and D. D. DesMarteau, *J. Am. Chem. Soc.*, **98**, 3529 (1976).
- 2 A. Sekiya and D. D. DesMarteau, *J. Fluorine Chem.*, **15**, 183 (1980).
- 3 R. P. Hirsehmann, H. L. Simon and D. E. Young, *Spectrochim. Acta.*, **27A**, 421 (1971).
- 4 S. C. Chang, R. M. Hammaker and D. D. DesMarteau, to be published.
- 5 D. H. Dybvig, *Inorg. Chem.*, **5**, 1795 (1966).
- 6 J. A. Young, S. N. Tsoukalas and R. D. Dresdner, *J. Am. Chem. Soc.*, **80**, 3604 (1958).
- 7 S. C. Chang and D. D. DesMarteau, *J. Am. Chem. Soc.*, submitted for publication.