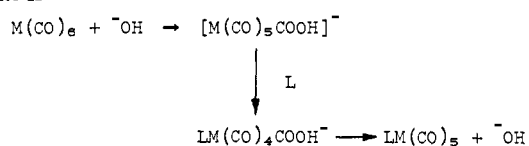


Scheme II



beled species when carried out in the presence of isotopically enriched hydroxide ion. Figure 2 illustrates the ν_{CO} infrared spectra obtained employing the Hui and Shaw¹⁹ preparation in $^{18}\text{OH}^-$ when L = diphos (1,2-bis(diphenylphosphino)ethane). These spectra indicate the oxygen label to be equally distributed between the axial and equatorial carbonyl positions. The oxygen label was indeed confirmed to be statistically distributed in the $\text{W}(\text{CO})_4(\text{diphos})$ derivative by the ^{17}O NMR spectrum of a sample prepared in the presence of H_2^{17}O .²⁰

In conclusion, since the oxygen-exchange reaction of the group 6b metal hexacarbonyls is so facile, to prepare specifically labeled derivatives of substituted metal carbonyls, it is necessary to carry out the enrichment on the substituted metal carbonyl species themselves.

Acknowledgment. The financial support of the National Science Foundation through Grant CHE 76-04494 is greatly appreciated.

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- (10) See for example the procedure employed in ref 3.
- (11) (a) Because the $\text{LFe}(\text{CO})_4$ species are fluxional^{11b-c} it is impossible to assess the site of initial attack in these derivatives, although there are other indications which suggest that the attack on $\text{LFe}(\text{CO})_4$ by nucleophiles is at an axial carbonyl ligand.^{11d} (b) O. A. Gansow, A. B. Burke, and W. O. Vernon, *J. Am. Chem. Soc.*, **94**, 2550 (1972). (c) F. A. Cotton and J. M. Troup, *ibid.*, **96**, 3438 (1974). (d) M. Y. Darensbourg, H. L. Conder, D. J. Darensbourg, and C. Hasday, *ibid.*, **95**, 5919 (1973).
- (12) Under the reaction conditions given above $\text{Cr}(\text{CO})_4(\text{diphos})$ was observed not to undergo oxygen exchange over prolonged reaction periods.
- (13) J. E. Gordon and R. E. Kutina, *J. Am. Chem. Soc.*, **99**, 3903 (1977).
- (14) Indications are that these processes are indeed fast relative to the chemical factors.¹³
- (15) See review by F. Calderazzo on metal carbonyls in I. Wender and P. Pino, "Metal Carbonyls in Organic Synthesis", Interscience, New York, N.Y., 1968.
- (16) We have no evidence for the details of the last step in this process; i.e., the reaction between $[\text{M}(\text{CO})_5\text{H}]^-$ with $\text{M}(\text{CO})_6$ is only conjecture.
- (17) In general, these derivatives are believed to be relatively unstable with respect to dimer disruption.¹⁸
- (18) (a) M. Y. Darensbourg, N. Walker, R. R. Burch, Jr., *Inorg. Chem.*, in press; (b) M. Y. Darensbourg and N. Walker, *J. Organomet. Chem.*, **117**, C68 (1976).
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- (20) Two equal intensity signals were observed in the CO region at 358.0 and 348.7 ppm relative to H_2^{17}O . ^{17}O NMR results were obtained by L. J. Todd and J. P. Hickey, Indiana University.

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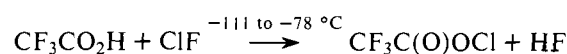
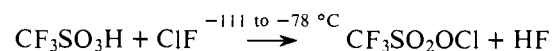
Received October 6, 1977

Chlorine(I) Derivatives of Trifluoromethanesulfonic Acid and Trifluoroacetic Acid

Sir:

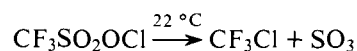
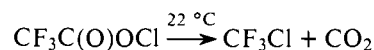
Halogen (Cl, Br, I) derivatives of strong oxy acids are exceedingly powerful electrophilic halogen sources. Their

properties and utility as synthetic reagents are exemplified by the halogen fluorosulfates $\text{XOSO}_2\text{F}^{1-4}$ and pentafluororhotoselenates XOSeF_5 .^{4,5} The chlorine(I) and bromine(I) derivatives are the most useful for synthesis. Two strong acids, whose halogen derivatives ($\text{X} = \text{Cl}, \text{Br}$) have not been previously reported, are $\text{CF}_3\text{SO}_3\text{H}$ ⁶ and $\text{CF}_3\text{CO}_2\text{H}$.^{7,8} Derivatives of both acids are of course well known and large in number.⁹⁻¹⁰ However, the lack of a suitable strong oxidizing agent containing these groups limits the scope of their chemistry. We have prepared both $\text{CF}_3\text{SO}_2\text{OCl}$ and $\text{CF}_3\text{C}(\text{O})\text{OCl}$ by the low temperature reaction of the acids with chlorine monofluoride.



The reactions are carried out in Kel-F reactors by condensing the ClF onto the acid at -196°C and warming slowly from -111 to -78°C , followed by several hours at -78°C . On a 10-mmol scale the reactions are quantitative yielding a pale yellow liquid and a colorless layer of HF. The HF is removed from $\text{CF}_3\text{SO}_2\text{OCl}$ by pumping at -78°C . For $\text{CF}_3\text{C}(\text{O})\text{OCl}$, the mixture is transferred onto NaF at -196°C through a short connection as the reactor warms slowly from -78°C . Pure $\text{CF}_3\text{C}(\text{O})\text{OCl}$ is then collected at -111°C by pumping through traps at -60 , -111 and -196°C as the NaF container warms slowly from -78°C .

Both compounds are somewhat unstable at 22°C and $\text{CF}_3\text{C}(\text{O})\text{OCl}$ will explode if the pressure of the gas exceeds ~ 50 Torr.



The compounds have been characterized by their reaction stoichiometry, by quantitative decomposition, and by their NMR and Raman spectra. Their ^{19}F NMR shows a singlet at δ 73.52 ($\text{CF}_3\text{SO}_2\text{OCl}$) and 70.94 ($\text{CF}_3\text{C}(\text{O})\text{OCl}$) relative to CFCl_3 as an external and internal standard, respectively. The identification of $\nu(\text{OCl})$ is easily made by comparing the liquid Raman spectra of the acid and chlorine derivative under identical conditions. It is an intense polarized band at 688 ($\text{CF}_3\text{SO}_2\text{OCl}$) and 716 cm^{-1} ($\text{CF}_3\text{C}(\text{O})\text{OCl}$). The complete spectra are consistent with that of other covalent compounds containing these groups.

In spite of their instability, these new chlorine derivatives can be readily prepared and used as reagents. The main difficulty in carrying out reactions of the compounds is to estimate the amount of hypochlorite. For $\text{CF}_3\text{SO}_2\text{OCl}$, reactions are normally carried out in the same vessel used for preparation, assuming quantitative formation from the acid. Alternatively, the compound can be vacuum transferred from a vessel at -40 to one at -196°C via a short connection. In the case of $\text{CF}_3\text{C}(\text{O})\text{OCl}$, the total, combined $\text{CO}_2/\text{CF}_3\text{Cl}$ pressure from purification and manipulation can be used to estimate the amount of the hypochlorite. The compound can be readily vacuum transferred from a vessel at -60 to one at -196°C via a short path. After transfer, the $\text{CF}_3\text{CO}_2\text{Cl}$ can be warmed to -111°C and the CO_2 and CF_3Cl removed and measured. Clearly, both compounds must be stored at low temperature ($\leq -78^\circ \text{C}$) and all reactions and manipulations conducted with proper shielding.

We are currently investigating their chemistry and find they add readily to unsaturated organic and inorganic substrates. In addition, $\text{CF}_3\text{SO}_2\text{OCl}$ is so powerful a Cl^+ source that it readily undergoes reaction with covalent chlorides to form Cl_2

and the trifluoromethanesulfonates. In our opinion, $\text{CF}_3\text{SO}_2\text{OCl}$ is the most electrophilic chlorine compound ever prepared and is probably more electrophilic than ClOSO_2F .

Acknowledgment. Support of this work by the National Science Foundation is gratefully acknowledged.

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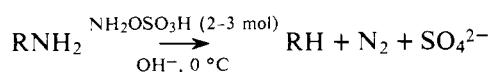
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A Direct, Selective, and General Method for Reductive Deamination of Primary Amines

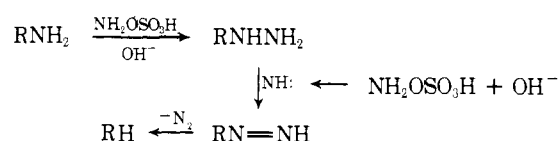
Sir:

We wish to report the first direct, selective, and general method for replacement of organic primary amino groups by hydrogen. This method is apparently applicable to a variety of structural types, including amines containing other functionalities.¹



In a representative example, 6-aminocaproic acid (2.62 g, 20 mmol) is dissolved in 40 mL of 2.5 M aqueous NaOH in a flask connected to a gas buret. To this is added hydroxylamine-*O*-sulfonic acid (HOS, 4.52 g, 95% pure, 38 mmol) and the mixture is stirred (magnetic stirrer) in an ice bath. After 35 min, an additional 2.26 g of HOS (19 mmol) and 20 mL of 2.5 M NaOH is added and stirring is continued until gas evolution almost stopped (90 min, volume of gas evolved was 110% of theory). Acidification with sulfuric acid, extraction with diethyl ether, and distillation of the extract gives 1.22 g (55% of theory) of caproic acid, bp 205-207 °C, characterized by elemental analysis and ¹H NMR. Table I lists other examples of the method conducted under similar conditions. The outline of a mechanism (shown in Scheme I) is suggested. N-Amination of amines to hydrazines by HOS under basic conditions (employing in general 3-5 mol of amine/mol of HOS) is a general reaction with established preparative utility.³ Formation of nitrene NH: from HOS with base has been proposed from successful trapping experiments with butadiene to yield

Scheme I



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Table I

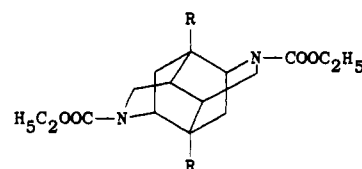
Substrate	Product	% yield ^a
2-Aminobenzoic acid	Benzoic acid ^b	72
2-Amino-3-methylbenzoic acid	3-Methylbenzoic acid	26 ^c
Benzylamine	Toluene	65 ^d
3-Aminopropionic acid	Propionic acid	50 ^d
Alanine	Propionic acid	50 ^d
L-Alanyl-L-phenylalanine	<i>N</i> -Propionyl-L-phenylalanine	51
1^e	2^f	49

^a Yields are those of pure, isolated products, unless otherwise noted.

^b Reaction finished at 90 °C. ^c 47% of starting material was recovered.

^d Yields were estimated by ¹H NMR analysis of reaction mixture.

^e See Figure 1. ^f Figure 1.

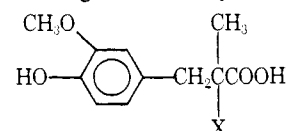


1, R = CH_2NH_2 (Ref. 2) **2**, R = CH_3

Figure 1.

pyrroline.⁴ The facile conversion of $\text{RN}=\text{NH}$ to RH and N_2 is well recognized.⁵ Further evidence for the above mechanism was provided by treatment of benzylhydrazine or *p*-hydrazinobenzoic acid with HOS under the conditions described above, to furnish toluene (73% yield, besides 10% bibenzyl) or benzoic acid (41%), respectively.⁶

Substitution of primary amino groups contained in natural products (e.g., in amino acids, amino sugars, peptides, and proteins) by hydrogen (deuterium, tritium) appears to be an especially attractive field for application of this method. **3** ((*S*)-4-hydroxy-3-methoxy- α -methylphenylalanine⁷) was "deuterodeaminated" to give **4** in 31% yield. The labile protons



3, X = NH_2
4, X = D
5, X = H

of **3** and HOS were first exchanged for deuterium with D_2O (20 vol of D_2O was employed, followed by evaporation in vacuo to dryness; this treatment was repeated). NaOD in D_2O was obtained from Merck-Canada. **4**: ¹H NMR δ 1.16 (s, α - CH_3), 2.6 (d, $J = 7$ Hz, β -H), 2.94 (d, $J = 7$ Hz, β -H), 3.82 (s, OCH_3), 6.5-6.9 (m, aromatic H); mass spectrum *m/e* 211, 137 (4-hydroxy-3-methoxybenzyl), <2% of *m/e* 138. Reductive deamination of **3** in H_2O gave **5**, with $[\alpha]_D +2.1 \pm 0.5^\circ$ (*c* 1, in CHCl_3). Reductive deamination of **3** in methanol- $(\text{CH}_3)_4\text{N}^+\text{OH}^-$ (instead of H_2O -NaOH) gave **5** with $[\alpha]_D +5.6 \pm 0.5^\circ$ (*c* 1, in CHCl_3). This dependence of stereoselectivity on experimental conditions, as well as the low degree of stereoselectivity,⁸ suggests complex mechanism. **5**: ¹H NMR δ 1.16 (d, $J = 7$ Hz, α - CH_3), 2.32-3.06 (m, α -H and β -H), 3.82 (s, CH_3O -), 6.5-6.9 (m, aromatic H); mass spectrum *m/e* 210, 137.

The name "hydrodeamination" is proposed for this method.

References and Notes

- (1) (a) Transformation of some *unsubstituted* primary amines into the corresponding hydrocarbons by reaction with difluoroamine HNF_2 has already