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Rhodium-Mediated Insertion of CF_3-Substituted Carbenoid into O-H: An Efficient Method for the Synthesis of α-Trifluoromethylated Alkoxy- and Aryloxyacetic Acid Derivatives

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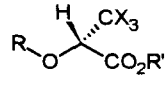
Abstract: CF_3-substituted diazo compound **2** undergoes a facile rhodium carbenoid mediated O-H insertion reaction with a variety of alcohols and phenols to afford the title compounds in good yield. Use of the title compounds as synthetic precursors for other fluorinated molecules is exemplified by the transformation of the product **3b** into β, β-difluoro- α-ketoester **5** and α-hydroxyketone **8**.

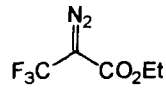
α-Methyl-substituted alkoxy- and aryloxyacetic acid derivatives, namely lactic acid derivatives, are a class of compounds that have found many important applications such as their use as herbicides[1] or chiral dopants for ferroelectric liquid crystals[2]. For example, several α-methyl aryloxyacetic acid derivatives **1** (X = H, R = aryl, R′ = H or Et) known as Mecoprop, Diclofop, Pyrenifop, and Fluazifop, etc. represent a commercially important class of herbicides. Substitution of a methyl by a trifluoromethyl group in organic molecules may lead to a significant change in their biological and physical properties[3]. Based on this knowledge, it was considered worthwhile to develop a simple method for the preparation of α-trifluoromethylated alkoxy- and aryloxyacetic acid derivatives **1** (X = F). Until now, no general method for the synthesis of this type of fluorinated compounds has been developed. It was expected that the general method for the synthesis of the nonfluorinated compounds, which is based on the nucleophilic displacement of a halogen atom from 2-halogenopropanoate with alkoxide or aryloxide, would not be suitable. The difficulties encountered in the S_N2 substitution at a carbon center bearing a trifluoromethyl group[4] as well as the preparation of the requisite fluorinated precursors were considered to be the main problems.



1

In recent years, synthetic use of diazo compounds in organic chemistry has increased dramatically as a result of the development of new transition metal catalysts in lieu of the classical heterogeneous copper

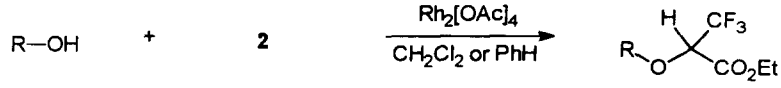
catalysts[5]. Our own interest in this field focuses on the synthesis of diazo compounds bearing a trifluoromethyl group and their use in organofluorine synthesis through transition metal catalyzed decomposition[6]. In our studies, advantage has been taken of the trifluoromethyl group which can, on one hand, act as an electron withdrawing group necessary for the stabilization of the diazo group and, on the other hand, avoids the problem of 1,2-hydrogen shifts commonly encountered in cases where the carbenoid carbon is substituted by a simple alkyl group[7]. We report here that an O-H insertion reaction of a trifluoromethyl-substituted rhodium carbenoid derived from the diazo compound **2** could be successfully employed to prepare α-trifluoromethylated alkoxy and aryloxyacetic acid derivatives.



2

Reactions involving O-H insertion have been investigated under photochemically and copper or rhodium catalyzed conditions[5]. Catalysis by rhodium was considered to be the best way in terms of mild reaction conditions and effectiveness[8]. The reaction of diazo compound **2** with various hydroxylic compounds using rhodium acetate as catalyst was studied (Scheme 1). The decomposition of the diazo compound **2** in dichloromethane or benzene resulted in smooth evolution of nitrogen. The trifluoromethyl-substituted rhodium carbenoid thus generated underwent O-H insertion with a variety of alcohols and phenols to give the corresponding insertion products in moderate to good yield. With unsaturated alcohols as the substrates, no products resulting from the cyclopropanation of the double bond were observed. When the reaction is extended to an optically active alcohol, i.e. menthol (entry 6, table 1), a moderate asymmetric induction at the carbenoid carbon was observed. The diastereomeric ratio of the product was found to be 80 : 20. This observation complements the result recently published by *Moody et al.* who studied the diastereoselectivity of rhodium-catalyzed carbenoid O-H insertion with a chiral auxiliary, e.g. a menthyl group, placed in the carbenoid moiety[9].

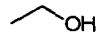
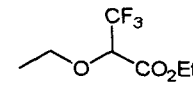
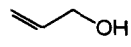
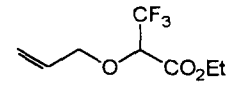
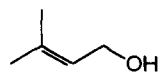
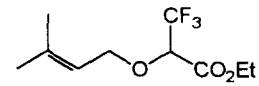
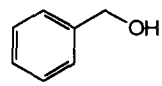
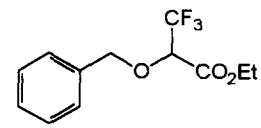
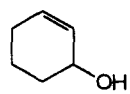
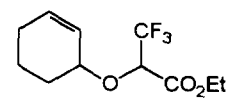
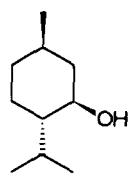
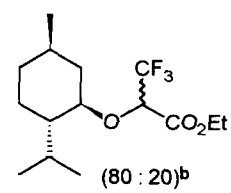
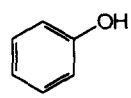
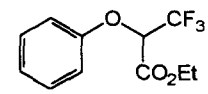
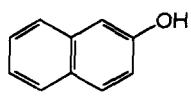
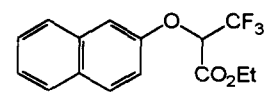
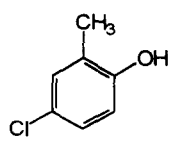
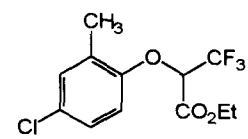
Scheme 1



3

Of particular interest is the synthesis of α-trifluoromethylated phenoxy- and naphthoxyacetic acids based on the the known important biological activity of the corresponding α-methyl-substituted compounds **1** (X = H). A trifluoromethyl instead of a methyl group at the α-position of these aryloxy substituted acetic acid derivatives might act as a more effective blocking group[3] and hence lead to the development of more active herbicides. For comparison, the fluorinated analogue of Mécoprop **3i** was synthesized (entry 9, table 1)

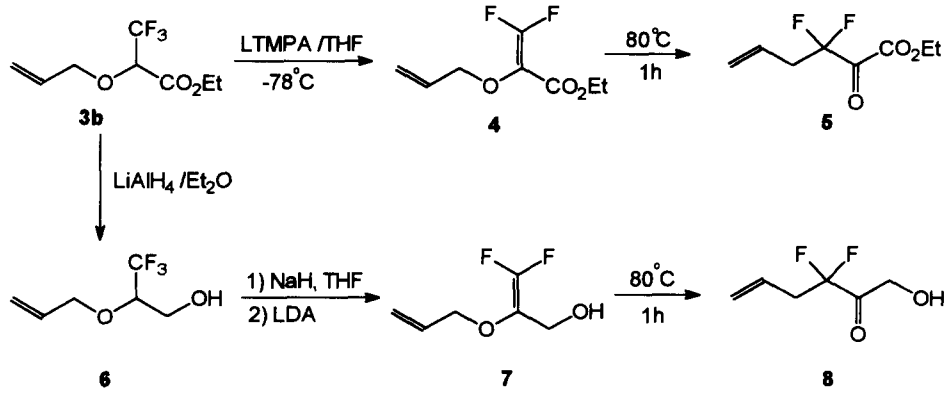
Table 1 Rhodium catalyzed insertion of CF_3-carbenoid into O-H of alcohols and phenols

Entry	R—OH	Conditions[a]	Products	Yield[c]
1		CH_2Cl_2/40℃	 **3a**	72%
2		CH_2Cl_2/40℃	 **3b**	75%
3		CH_2Cl_2/40℃	 **3c**	78%
4		CH_2Cl_2/40℃	 **3d**	70%
5		CH_2Cl_2/40℃	 **3e**	81%[d]
6		CH_2Cl_2/40℃	 (80 : 20)[b] **3f**	64%
7		PhH/25℃	 **3g**	63%
8		PhH/60℃	 **3h**	56%
9		PhH/25℃	 **3i**	67%

(a) 1.0 % mol of $[Rh(AcO)_2]_2$ and 2.0 equivalents of alcohol or phenol are used for all reactions. (b) Refered to diastereoisomeric ratio measured by capillary GC, We are not yet able to assign the absolute configuration of the major isomer. (c) Yields of isolated products based on **2**. (d) 1:1 diastereoisomer mixture.

Finally, it is worthwhile to point out that the development of the described method for the synthesis of the title compounds has been additionally justified by their potential as intermediates for the synthesis of other functionalized organofluorine compounds. Thus, as an example of their useful applications, compound **3b** was treated with lithium 2,2,6,6-tetramethylpiperidide[10] and a potential *Claisen* rearrangement precursor **4** was obtained after β-elimination of fluoride from the corresponding α-deprotonated intermediate. Being facilitated by the two fluorine substituents[11], the *Claisen* rearrangement of **4** took place readily at 80 °C to afford the β,β-difluoro ketoester **5** in 63% overall yield. As similar transformation, starting with the alcohol **6**, obtained after lithium aluminum hydride reduction of compound **3b**, furnished an α,α-difluoro-α'-hydroxyketone **8** in 85% overall yield. Both of the difluorinated compounds **5** and **8** may serve as useful precursors for the synthesis of biologically interesting compounds bearing a difluoromethylene unit.

Scheme 2



In summary, we have achieved an efficient synthesis of a variety of α-trifluoromethylated alkoxy- and aryloxyacetic acid derivatives via rhodium catalyzed O-H insertion reaction of a CF_3-carbenoid with alcohols and phenols. The title compounds are not only of potential practical utilities but also useful intermediates suitable for further synthetic elaboration.

Experimental Section

^{1}H NMR spectra were recorded on a Varian JEOL FX-90 or a Bruker AM-300 spectrometer with Me_4Si as internal standard. ^{19}F NMR spectra were obtained on a Varian EM-360L spectrometer using trifluoroacetic acid as external standard; downfield shifts were designated as negative. Mass spectroscopy was conducted on a Finnigan 4021 GC/MS/DC spectrometer and elemental analysis were carried out using a Perkin-Elmer Elemental analyser 2450 CHN instrument. All reactions were routinely monitored with the aid of TLC or ^{19}F NMR spectroscopy.

Benzene was dried over sodium wire and CH_2Cl_2 was distilled from P_2O_5. Diethyl ether and THF were distilled from sodium benzophenone ketyl before use. Diazo compound **2** was prepared as described in our provious publication[6c].

Rhodium catalyzed O-H insertion reaction, general procedure: To a solution of the alcohol or phenol (40 mmol) and rhodium acetate (0.2 mmol) in CH_2Cl_2 or benzene (20 mL) was added the diazo compound **2** (20 mmol) in the corresponding solvent (10 mL) over a period of 1h . After the addition was completed, the reaction mixture was stirred for an additional 30 min. The volatiles were removed *in vacuo* and the residue was subjected to column chromatography on silica gel using a mixture of petroleum ether (60-90 °C) and ethyl acetate as the eluent.

Ethyl 2-ethoxy-3,3,3-trifluoropropanoate (3a): ^{1}H NMR ($CDCl_3$) δ 4.33(m, 2H), 4.25(q, J = 6.7Hz, 1H), 3.74(m, 2H), 1.32(t, J = 7.1Hz, 3H), 1.30(t, J=7.1Hz, 3H); ^{19}F NMR ($CDCl_3$) δ -4.0(d, J = 6.7Hz); MS (EI, m/z) 201(M^++1, 100), 173(13), 59(31), 43(15). Anal. Calcd for $C_7H_{11}F_3O_3$: C, 42.01; H, 5.54. Found: C, 41.90; H, 5.68.

Ethyl 2-(propenyloxy)-3,3,3-trifluoropropanoate (3b): ^{1}H NMR ($CDCl_3$) δ 5.89(m, 1H), 5.02(m, 2H), 4,41(q, J = 6.5Hz, 1H), 4.36(q, J = 7.1Hz, 2H), 4.24(d, J = 7.2Hz, 2H), 1.34(t, J = 7.1Hz, 3H); ^{19}F NMR ($CDCl_3$) δ -3.6(d, J = 6.5Hz); MS (EI, m/z) 213(M^++1, 100), 183(16), 166(45), 59(25). Anal. Calcd for $C_8H_{11}F_3O_3$: C, 45.29; H, 5.23. Found: C, 45.60; H,5.28.

Ethyl 2-(3-methyl-2-butenyloxy)-3,3,3-trifluoropropanoate (3c): ^{1}H NMR ($CDCl_3$) δ 5.33(m, 1H), 4.40(q, J = 6.5Hz, 1H), 4.35(q, J = 7.1Hz, 2H), 4.30(dd, J = 7.4Hz, 12.1Hz, 1H), 4.22(dd, J = 7.4Hz, 12.1Hz, 1H), 1.73(s, 3H), 1.82(s, 3H), 1.33(t, J = 7.1Hz, 3H); ^{19}F NMR ($CDCl_3$) δ -3.5(d, J = 6.5Hz); MS (EI, m/z) 241(M^++1, 52), 212(12), 195(100), 168(31), 69(42). Anal. Calcd for $C_{10}H_{15}F_3O3$: C, 50.00; H,6.29. Found: C, 49.98; H, 6.01.

Ethyl 2-benzyloxy-3,3,3-trifluoropropanoate (3d): ^{1}H NMR ($CDCl_3$) δ 7.31(s, 5H), 4.78(d, J = 12.0Hz, 1H), 4.57(d, J = 12.0Hz, 1H), 4.41(q, J = 6.8Hz, 1H), 4.32(m, 2H), 1.30(t, J = 7.1Hz, 3H); ^{19}F NMR ($CDCl_3$) δ -3.9(d, J = 6.8Hz); MS (EI, m/z) 263(M^+, 14), 233(12), 217(18), 91(100). Anal. Calcd for $C_{12}H_{13}F_3O_3$: C, 54.96; H, 5.00. Found: C, 55.17; H, 5.21.

Ethyl 2-(2-cyclohexenyloxy)-3,3,3-trifluoropropanoate (3e): ^{1}H NMR ($CDCl_3$) δ 5.70-5.90(m, 2H), 4.40(q, J = 6.7Hz, 1H), 4.33(m, 2H), 4.25(m, 1H), 1.92-2.13(m, 2H), 1.55-1.75(m, 4H), 1.30(t, J = 7.1Hz, 3H); ^{19}F NMR ($CDCl_3$) δ -3.4(d, J = 6.7Hz), -3.3(d, J = 6.7Hz); MS (EI, m/z) 252(M^+, 23), 223(19), 206(45), 81(100). Anal. Calcd for $C_{11}H_{15}F_3O_3$: C, 52.38; H, 5.99. Found: C, 52.52; H, 6.07.

Ethyl 2-[(1R, 2S, 5R)-(-)-menthyl]oxy-3,3,3-trifluoropropanoate (3f): ^{1}H NMR ($CDCl_3$) δ 4.40(q, J = 6.7Hz, 1H), 4.30(q, J = 7.1Hz, 2H), 3.35(dt, J = 4.0Hz, 8.0Hz, 0.2 × 1H), 3.29(dt, J = 4.2Hz, 8.7Hz, 0.8 × 1H), 2.35(m, 1H), 2.05(m, 0.8 × 1H), 1.90(m, 0.2 × 1H), 1.67(m, 1H), 1.32(t, J = 7.1Hz, 3H), 0.93(d, J = 6.6Hz, 3H), 0.88(d, J = 7.1Hz, 3H), 0.82-1.05(m, 6H), 0.72(d, J = 6.9Hz, 3H); ^{19}F NMR ($CDCl_3$) δ -3.5(d, J = 6.7Hz); MS (EI, m/z) 310(M+, 5), 225(26), 197(19), 155(31), 123(50), 95(84), 81(100)., Anal. Calcd for $C_{15}H_{25}F_3O_3$: C, 58.05; H,8.12. Found: C, 58.31; H, 8.46.

Ethyl 2-phenyloxy-3,3,3-trifluoropropanoate (3g): ^{1}H NMR (CCl_4) δ 6.82-7.40(m, 5H), 4.89(q, J = 6.4Hz, 1H), 4.30(q, J = 7.1Hz, 1H), 1.29(t, J = 7.1Hz, 3H); ^{19}F NMR (CCl_4) δ -4.3(d, J = 6.4Hz); MS (EI, m/z) 248(M^+, 41), 175(32), 77(100). Anal. Calcd for $C_{11}H_{11}F_3O_3$: C, 53.23; H, 4.47. Found: C, 52.85; H, 4.36.

Ethyl 2-(2-naphthyloxy)-3,3,3-trifluoropropanoate (3h): ^{1}H NMR (CCl_4): δ 7.4-7.32(m, 3H), 6.90-7.40(m, 4H), 4.92(q, J = 6.2Hz, 1H), 4.20(q, J = 7.1Hz, 2H), 1.20(t, J = 7.1Hz, 3H); ^{19}F NMR (CCl_4): δ -4.0(d, J = 6.2Hz); MS (EI, m/z) 298(M^+, 100), 225(12), 127(47), 115(39). Anal. Calcd for $C_{15}H_{13}F_3O_3$: C, 60.41; H, 4.39. Found: C, 60.51; H,4.24.

Ethyl 2-(2-methyl-4-chlorophenyloxy)-3,3,3-trifluoropropanoate (3i): ^{1}H NMR ($CDCl_3$) δ 7.19(d, J = 2.9Hz, 1H), 7.10(dd, J = 8.7Hz, 1H), 6.65(d, J = 8.7Hz, 1H), 4.92(q, J = 6.4Hz, 1H), 4.32(m, 2H), 2.29(s, 3H), 1.30(t, J = 7.2Hz, 3H); ^{19}F NMR ($CDCl_3$) δ -4.0(d, J = 6.4Hz); MS (EI, m/z) 296(M^+, 65), 223(38), 141(100), 125(73). Anal. Calcd for $C_{12}H_{12}F_3ClO_3$: C, 48.58; H, 4.08. Found: C, 48.67; H, 3.85.

Conversion of the insertion product 3b to β,β-difluoro-α-oxoester 5: A solution of lithium 2,2,6,6-tetramethylpyperidide, prepared by mixing a hexane solution of butyllithium (1.3M, 7.7mL,10 mmol) and 2,2,6,6-tetramethylpiperidine (1.4 g, 10 mmol) in diethyl ether (20 mL), was added over 30 min. to compound **3b** (2.1 g, 10 mmol) in ether cooled at -78 °C. The reaction mixture was left at - 78 °C for additional 30 min. before it was poured into diluted hydrochloric acid solution (0.5N, 50 mL). After usual work-up, the crude product was dissolved in benzene and heated under reflux for 1 h. The solvent was evaporated and the residue chromatographed on silica gel eluting with a 2:8 mixture of ethyl acetate and potroleum ether to give 1.2 g (63%) of **5** as an oil.

Ethyl 2-(2-propenyloxy)-3,3-difluoropropenoate (4): ^{1}H NMR (CCl_4): δ 5.85(m, 1H), 5.2(m, 2H), 4.35(d, J = 6.2Hz, 2H), 4.30(q, J = 7.1Hz, 2H), 1.31(t, J = 7.1Hz, 3H); ^{19}F NMR (CCl_4) δ 4.0(d, J = 15.5Hz), 9.5(d, J = 15.5Hz); MS (EI, m/z) 193(M^++1, 19), 173(9), 165(47), 91(100).

Ethyl 3,3-difluoro-2-oxo-5-hexenoate (5): ^{1}H NMR ($CDCl_3$) δ 5.8(m, 1H), 5.2(m, 2H), 4.30(q, J = 7.1Hz, 2H), 2.81(dt, J = 18.5Hz, 7.0Hz, 2H), 1.31(t, J = 7.1Hz, 3H); ^{19}F NMR ($CDCl_3$) δ 35.8(t, J = 18.5Hz); MS (EI, m/z) 193(M^++1, 9), 145(32), 137(13), 91(100). Anal. Calcd for $C_8H_{10}F_2O_3$: C, 50.00; H, 5.25. Found: C, 49.66; H, 5.47.

2-(2-Propenyloxy)-3,3,3-trifluoropropanol (6): A solution of compound **3b** (4.2 g, 20 mmol) in diethyl ether (20 mL) was added over 20 min. to an ethereal suspension of $LiAlH_4$ (0.32 g, 10 mmol) cooled with an ice bath. The reaction mixture was stirred at room temperature for 4h and worked up as usual. The product was isolated by distilation in 78% yield. ^{1}H NMR ($CDCl_3$) δ 5.82(m, 1H), 5.12(m, 2H), 4.35(dd, J = 11.4Hz, 6.9Hz, 1H), 4.18(dd, J = 11.4Hz, 7.6Hz, 1H), 3.70-3.94(m, 3H); ^{19}F NMR ($CDCl_3$) δ -2.7 (m); MS (EI,

m/z) 170(M^+, 5), 152(32), 141(15), 41(100). Anal. Cacld for $C_6H_9F_3O_2$: C, 42.36; H, 5.33. Found: C, 42.56; H, 5.29.

Conversion of compound 6 to fluorinated hydroxyketone 8: A solution of lithium diisopropylamide, prepared by mixing butyllithium (1.3M in hexane, 12 mL, 15 mmol) and diisopropylamine (2.0 mL, 15 mmol) in THF, was added to a solution of sodium alcoholate in THF prepared from the alcohol **6** (1.5 g, 10 mmol) and NaH (0.23 g, 10 mmol). The reaction mixture was kept at -78 °C for 2h, gradually warmed to -30 °C over 1h and finally poured into hydrochloric acid (0.5*N*, 60 mL). Usual work-up give a crude product whose NMR spectral data corresponded to compound **7**. Without further purification, this crude product was taken up in benzene and heated at reflux for 1h. After evaporation of the solvent, the residue was subjected to chromatography using a 3:7 mixture of ethyl acetate and petroleum ether as the eluent to give 1.3 g (85% based on **6**) of **8** as an oil.

2-(Propenyloxy)-3,3-difluoro-2-propenol (7): ^{1}H NMR ($CDCl_3$) δ 5.94(m, 1H), 5.12(m, 2H), 4.28(d, J = 7.0Hz, 2H), 4.09(m, 2H), 3.02(br. s, 1H); ^{19}F NMR ($CDCl_3$) δ 34.6(d, J = 69.0Hz), 23.2(d, J = 69.0Hz); MS (EI, m/z) 150(M^+, 20), 130(8), 127(25), 43(100).

1-Hydroxy-3,3-difluoro-5-hexen-2-one (8): ^{1}H NMR ($CDCl_3$) δ 5.85(m, 1H), 5.08 (m, 1H), 4.48(s, 2H), 3.05(br. s, 1H), 2.75(td, J = 18.0Hz, 7.0Hz, 2H); ^{19}F NMR ($CDCl_3$) δ 34.2(t, J = 18.0Hz); MS (EI, m/z) 150(M^+, 100), 130(24), 119(8), 41(60). Calcd. Anal for $C_6H_8F_2O_2$: C, 48.00; H, 5.37. Found: C, 48.32; H, 5.39.

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