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PREPARATION AND CARBONYL ADDITION OF γ,γ-DIFLUOROALLYLSILANES

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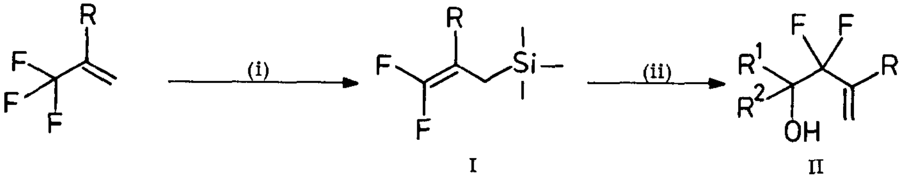
The reaction of 3,3,3-trifluoropropenes with disilane/tetrabutylammonium fluoride or silyllithium reagent gives γ,γ-difluoroallylsilanes which afford gem-difluoroallyl adducts of aldehydes and ketones with the aid of a catalyst such as potassium t-butoxide or tris(diethylamino)sulfonium difluorotrimethylsilicate.

In view of the rapidly expanding applications of organofluorine[1] and -silicon[2] reagents, preparation of silicon- and fluorine-containing synthetic reagents should be important. Of many organosilicon reagents allylsilanes are most versatile as these are transformed into allyl anion[3] or allyl cation[4] equivalents under mild conditions. Herewith we report the synthesis of γ,γ-difluoroallylsilanes and the addition of gem-difluoroallyl unit to aldehyde and ketone carbonyls.

Disilane/tetrabutylammonium fluoride (TBAF) reagent system is a silyl anion source having unique reactivity.[5] By applying the reagent to 3,3,3-trifluoropropene, we obtained γ,γ-difluoroallylsilanes under S_N2' type substitution as summarized in Table 1. Aprotic polar solvents such as hexamethylphosphoric triamide (HMPA) and 1,3-dimethyl-3,4,5,6-tetrahydro-2(1H)-pyrimidinone (DMPU) are found effective for the preparation. A less polar solvent tetrahydrofuran (THF) also is employed for the synthesis of Ia. Starting with pentamethylphenyldisilane, we always obtained dimethylphenylsilyl product owing to selective fluoride attack on the less hindered silicon atom of disilane to produce electronically favored dimethylphenylsilyl anion.[5] Silyllithium also is capable of the same substitution.[6] 2-Trifluoromethylpropene is transformed equally well into 1,1-difluoro-2-methyl-3-(dimethylphenylsilyl)propene (Ic).



(i) disilane/TBAF or ≡SiLi

(ii) TASF or tBuOK, R^1COR^2

Table 1 Synthesis of γ,γ-Difluoroallylsilanes

Starting Material	Reagent, Conditions	Product (% yield)[a]
CF_3-CH=CH_2	$PhMe_2SiSiMe_2Ph$/TBAF/DMPU	CF_2=$CHCH_2SiMe_2Ph$ (Ia) (84)
CF_3-CH=CH_2	$PhMe_2SiSiMe_2Ph$/TBAF/HMPA	Ia (85)
CF_3-CH=CH_2	$Me_3SiSiMe_2Ph$/TBAF/THF	Ia (85)
CF_3-CH=CH_2	$Me_3SiSiMe_2Ph$/TBAF/DMPU	Ia (66)
CF_3-CH=CH_2	$Me_3SiSiMe_2Ph$/TBAF/HMPA	Ia (64)
CF_3-CH=CH_2	$PhMe_2SiLi$/THF[b]	Ia (62)
CF_3-CH=CH_2	$Me_3SiSiPh_3$/TBAF/HMPA	CF_2=$CHCH_2SiPh_3$ (Ib) (56)[c]
CF_3-C(Me)=CH_2	$PhMe_2SiSiMe_2Ph$/TBAF/THF	CF_2=C(Me)CH_2SiMe_2Ph (Ic) (68)
CF_3-C(Me)=CH_2	$Me_3SiSiMe_2Ph$/TBAF/HMPA	Ic (74)[d]
CF_3-C(Me)=CH_2	$PhMe_2SiLi$/THF	Ic (71)

a) Isolated yields unless otherwise stated. b) See note 6. c) Estimated by ^{1}H NMR.
d) Reaction in THF gave no trace of the product.

Preparation of 1,1-Difluoro-3-(dimethylphenylsilyl)propene (Ia): A THF (2 ml) solution of pentamethylphenyldisilane (0.238 ml, 1 mmol) was treated with TBAF (0.5 M THF solution, 0.2 ml, 0.1 mmol). After 5 min 3,3,3-trifluoropropene (26.9 ml, 1 atm, 1.2 mmol) was bubbled at room temperature. The resulting reaction mixture was stirred for 6 h, then treated with water, and extracted with ether. The ethereal extract was washed with water, dried over magnesium sulfate, and concentrated. Distillation at 120-130°C (bath temp)/23 Torr gave Ia (181 mg, 85% yield) as a colorless oil. IR (neat): 1745, 1252, 1234, 895, 835 cm^{-1}; MS: m/z (rel %) 212 (M^+, 0), 135 (100), 107 (6), 105 (6), 77 (3), 43 (10); ^{1}H NMR (CCl_4): δ 0.40 (s, 6 H), 1.55 (d, J = 9 Hz, 2 H), 4.10 (ddt, J = 25, 2, 8 Hz respectively, 1 H), 7.20-7.70 (m, 5 H); ^{19}F NMR (CCl_4) δ (from $CFCl_3$) 89.85 (dd, J = 50.8, 2.0 Hz, 1 F), 93.00 (dd, J = 50.8, 25.1 Hz, 1 F). Found: C, 61.97; H, 6.40%. Calcd for $C_{11}H_{14}F_2Si$: C, 62.23; H, 6.65%.

Upon treatment with a catalytic amount of tris(dimethylamino)sulfonium difluorotrimethylsilicate (TASF)[7,9] or potassium t-butoxide,[8] gem-difluoroallyl unit of γ,γ-difluoroallylsilanes are found to add to carbonyl group of aldehydes and ketones as summarized in Table 2. Generally TASF catalyst is superior to potassium t-butoxide as TASF works under neutral conditions. TBAF turned out much less effective (THF reflux, 22% yield of Ia). For the reaction media aprotic polar solvents such as HMPA and DMPU as well as THF were effective. The relatively low yield of undecanal adduct may be

Table 2 Reaction of γ,γ-Difluoroallyl(dimethylphenyl)silanes with Aldehydes and Ketones

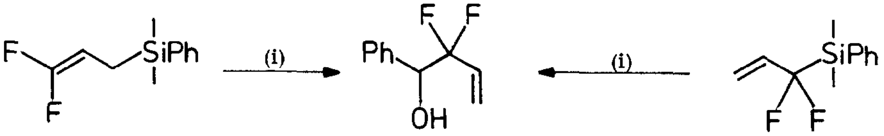
Run	Aldehyde or Ketone	Conditions[a]	Product (% yield)[b]
1	PhCHO	KOtBu (1.1 eq), HMPA	$PhCH(OH)CF_2CH{=}CH_2$ (IIa) (68)
2	PhCHO	KOtBu (1.1 eq), DMPU	IIa (68)
3	PhCHO	KOtBu (1.1 eq), THF/DMPU (2:1), -78°C - r.t.	IIa (50)
4	PhCHO	KOtBu, DMPU	IIa (98)
5	PhCHO	TASF, DMPU	IIa (93)
6	PhCHO	TASF, THF	IIa (100)
7	PhCHO	KOtBu, DMPU[c]	$PhCH(OH)CF_2C(Me){=}CH_2$ (IIb) (100)
8	PhCHO	TASF, DMPU[c]	IIb (98)
9	$p\text{-}ClC_6H_4CHO$	KOtBu, DMPU	$p\text{-}ClC_6H_4CH(OH)CF_2CH{=}CH_2$ (IIc) (87)
10	$p\text{-}ClC_6H_4CHO$	TASF, DMPU	IIc (100)
11	$p\text{-}BuOC_6H_4CHO$	KOtBu, DMPU	$p\text{-}BuOC_6H_4CH(OH)CF_2CH{=}CH_2$ (IId) (100)
12	Ph_2CO	TASF, THF	$Ph_2C(OH)CF_2CH{=}CH_2$ (IIe) (34)[d]
13	PhCH=CHCHO	TASF, DMPU	$PhCH{=}CHCH(OH)CF_2CH{=}CH_2$ (IIf) (52)
14	$n\text{-}C_{10}H_{21}CHO$	TASF, DMPU	$n\text{-}C_{10}H_{21}CH(OH)CF_2CH{=}CH_2$ (IIg) (44)
15	$n\text{-}C_{10}H_{21}CHO$	TASF, THF	IIg (42)
16	$t\text{-}C_4H_9CHO$	TASF, DMPU	$t\text{-}C_4H_9CH(OSiMe_2Ph)CF_2CH{=}CH_2$ (IIh) (53)[e]

a) Unless otherwise stated, Ia (1 eq) was employed for the difluoroallylation. Unless specified, the reaction was carried out at room temperature with 0.1 eq of KOtBu or 0.06 eq of TASF catalyst.
b) Isolated yield. c) Difluoroallylsilane Ic was used. d) Recovered benzophenone (50%).
e) Isolated as the dimethylphenylsilyl ether without acidic workup.

ascribed to enolate formation and subsequent side reaction. Catalysis by potassium t-butoxide resulted only in self-condensation of the aldehyde. 4-t-Butylcyclohexanone was recovered owing to the same bypath. The carbonyl addition was regioselective to take place invariably at the fluorine-substituted carbon like gem-difluoroallyllithium.[10]

Experimental Details for the Reaction of Run 4 of Table 2: A DMPU (1 ml) solution of potassium t-butoxide (12 mg, 0.11 mmol) was added to a DMPU (2 ml) solution of Ia (0.208 ml, 1.0 mmol) and benzaldehyde (0.102 ml, 1.0 mmol). The reaction mixture was stirred overnight at room temperature and then treated with 1 N hydrochloric acid. Extraction with ether, washing the ethereal extract with brine, drying the organic layer over magnesium sulfate, concentration in vacuo, followed by preparative TLC purification (hexane-ethyl acetate 3:1, R_f 0.55), gave IIa (180 mg, 98% yield). IR (neat): 3440, 1650, 1500, 1421, 1200, 1160, 1060, 995, 955, 852, 703, 637 cm^{-1}; MS: m/z (rel %) 184 (M^+, 0), 108 (9), 107 (100), 79 (68), 77 (36), 51 (14); ^1H NMR (CCl_4): δ 3.59 (d, J = 5 Hz, 1 H), 4.79 (dt, J = 5, 10 Hz, 1 H), 5.34-6.18 (m, 3 H), 7.20-7.40 (m, 5 H); ^{19}F NMR (CCl_4): δ ($CFCl_3$) 105.87 (dt, J = 248, 10 Hz, 1 F), 110.65 (dt, J = 248, 10 Hz, 1 F). Found: C, 65.01; H, 5.41%. Calcd for $C_{10}H_{10}F_2O$: C, 65.21; H, 5.47%. Experiment of run 5 of Table 2 was carried out by adding TASF (20 mg, 0.06 mmol) to a mixture of Ia (0.208 ml, 1.0 mmol) and benzaldehyde (0.102 ml, 1.0 mmol) dissolved in DMPU (2 ml) and by allowing the reaction mixture to be stirred overnight at room temperature and gave IIa (0.172 g, 93% yield).

Since 3,3-difluoro-3-(dimethylphenylsilyl)propene (Id),[10] isomer of Ia, also gave exclusively IIa (58% yield) by the reaction with benzaldehyde (TASF catalyst), and since no interchange between these difluoroallylsilanes was observed under the reaction conditions, metal free gem-difluoroallyl anion might be involved for production of II, although gem-difluoroallyllithium exists only at low temperature of -95°C.[10]



Ia IIa Id

(i) PhCHO, TASF, DMPU

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