(Table 2) in the same direction.

We therefore conclude that the Diels–Alder reaction between diene and allenic ketones is a neutral electron demand type with matrix element control and the reactivity, the regio-and stereo-selectivities can be correctly accounted for using interaction energies calculated with the 4-center FMO formalism.

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Preparation of Allylic and Homoallylic Alcohols Containing Trifluoromethyl Group

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1,1,1-Trifluoro-4-substituted-3-buten-2-ols and 1,1,1-trifluoro-5-phenyl-4-penten-2-ol were prepared by hydromagnesation and palladium catalyzed phenylation in high stereoselectivity.

Introduction

A number of studies have been made on the biologically unique properties of trifluoromethylated organic compounds,[1] and several synthetic methods for these compounds have been developed in recent years. In order to introduce the trifluromethyl group into a carbon skeleton, fluorination of CO_2H by SF_4,[2,3] halogen exchange reactions,[4] and trifluoromethylation[5~7] have been suggested. However, such methods are sometimes accompanied by low reactivity and low selectivity. On the other hand, the use of a proper building block which already has the trifluoromethyl group attached is another promising approach. From this point of view, we have studied the synthesis of trifluoromethylated difunctional compounds.

Recently, we have reported the synthesis of 3-hydroxypropionic esters, allylic alcohols and homoallylic alcohols containing trifluoromethyl group, produced by the reaction of α,α,α-trifluoroacetaldehyde with organometals under ultrasonic irradiation.[8] In our continuing studies on the synthesis of building blocks containing the trifluoromethyl group, we here report the synthesis of substituted allylic and homoallylic alcohols containing trifluoromethyl group, which are interesting intermediates for heterocycles expected to be bioactive pharmaceuticals and agrochemicals.

Results and Discussion

Hydromagnesation of 1,1,1-Trifluoro-4-substituted-3-butyn-2-ol. We have attempted to design a synthetic route for α-trifluoromethyl allylic alcohols as shown in Scheme 1. The first step in Scheme 1 is to react lithium acetylides with α, α, α-trifluoroacetaldehyde at -78 °C to yield the corresponding 1,1,1-trifluoro-4-substituted-3-butyn-2-ol in good yield. Various spectral data that support the above structures are given in Table 1.

TABLE 1: Physical Properties of 1,1,1-Trifluoro-4-substituted-3-butyn-2-ol

R	Yield[a] (%)	bp (°C/mmHg)	^{19}F nmr[b] CF_3	^{1}H nmr -CH-
n-Bu	72	84/22	2.3 (d, J_{CF_3-CH}=5.65 Hz)	4.73 ppm
Ph	74	83/1.8	0.3 (d, J_{CF_3-CH}=4.4 Hz)	4.9

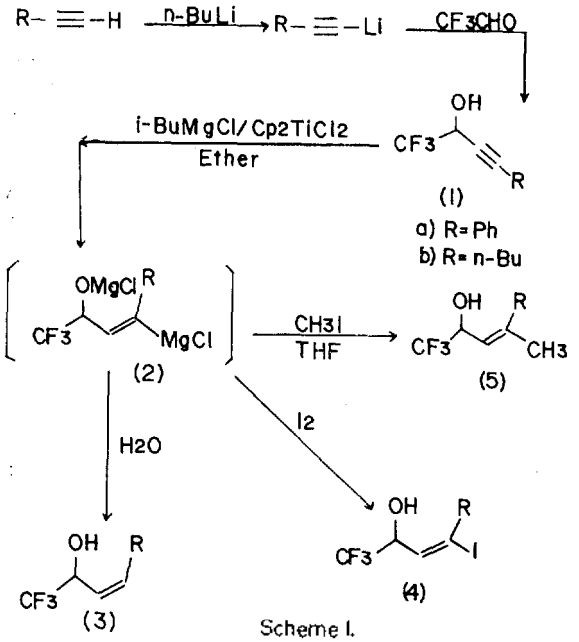
[a] Isolated yield. [b] δppm upfield from ext. CF_3CO_2H

It was reported that hydromagnesation of the carbon-carbon triple bond with iso-butylmagnesium chloride led to the functionalized carbon-carbon double bond with stereoselectivity.[9]

Thus, 1,1,1-trifluoro-4-substituted-3-butyn-2-ol (**1a**: R=phenyl, **1b**: R=*n*-butyl) reacted with 2.4 equiv. of iso-butylmagnesium chloride in the presence of 3 mol % Cp_2TiCl_2 in ether to afford 1,1,1-trifluoro-4-phenyl-3-buten-2-ol (**3a**, 100 % *Z*-form) and 1,1,1-trifluoro-3-octen-2-ol (**3b**, 100% *Z*-form) in 88 and 85% yield (isolated) respectively.

The above results strongly indicate that the hydromagnesation of the carbon-carbon triple bond proceeds to give *E*-type Grignard reagents containing trifluoromethyl group (**2**), which further react with several electrophiles to yield in high stereoselectivity the 4-substituted allyllic alcohols, (**3**), (**4**) and (**5**) as shown in Scheme 1.

Palladium-Catalyzed Phenylation. Another route to substituted allylic and homoallylic alcohols containing trifluoromethyl group is palladium catalyzed phenylation. The palladium-catalyzed phenylation is a very convenient method to form carbon-carbon bonds at unsubstituted vinylic positions. Recently, as an extension of catalytic arylation of olefins with aryl iodide in the presence of Pd(II) or Pd(O), the synthetically useful arylation of allylic alcohols has been reported by several groups, where ketones were obtained in high yields.[10~11]

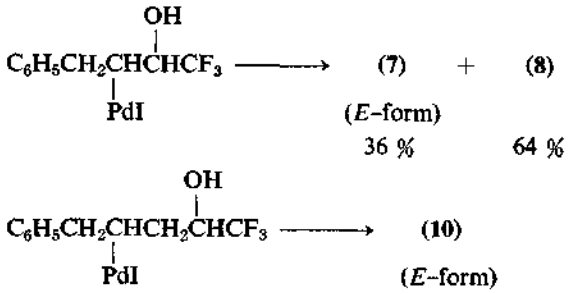


Scheme I.

In this context, we examined the phenylation of 1, 1, 1-trifluoro-3-buten-2-ol (**6**) and 1,1,1-trifluoro-4-pentene-2-ol (**9**) catalyzed by palladium acetate. (see Scheme 2)

When 1,1,1-trifluoro-3-buten-2-ol was heated with iodobenzene, triethylamine and palladium acetate in acetonitrile, ketone (**8**) was obtained as the major product (64%) along with the unsaturated alcohol (**7**, 36%, only *E*-form). In the case of 1,1,1-trifluoro-4-penten-2-ol (**9**), only unsaturated alcohol (**10**, only *E*-form) was formed at the same condition.

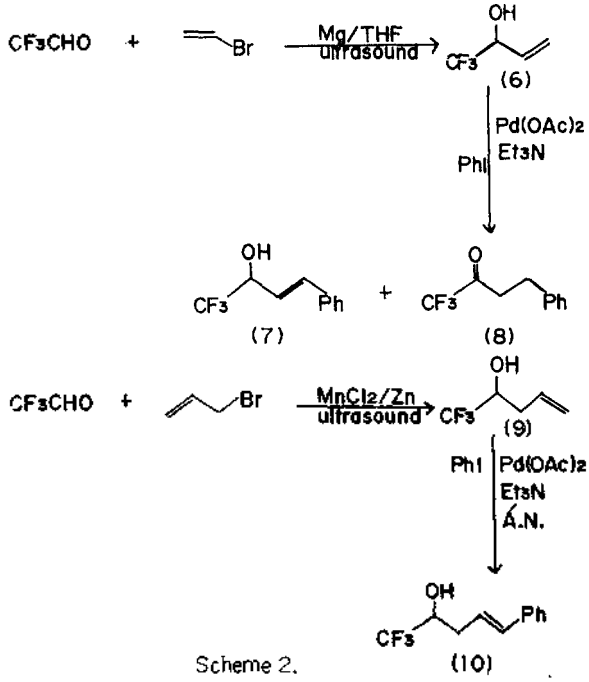
It is known that in the early stages of the reaction phenylpalladium iodide exists:[11] this could then add to the double bond of 1, 1, 1-trifluoro-3-buten-2-ol (**6**) and 1, 1, 1-trifluoro-4-penten-2-ol (**9**) via π-complex intermediate. The direction of addition of the phenyl group take place exclusively on the terminal olefinic carbon due to the electron withdrawing effect of trifluoromethyl group. (Nonfluorinated allylic and homoallylic alcohols gave 9% 2-arylation in allylic and 16% 3-arylation in homoallylic alcohols).[12,13] In the next step, *E*-elimination of HPdI could then afford (**7**), (**8**) and (**10**).



Trifluoromethyl group made it difficult to abstract the adjacent hydrogen, thus the formation of the ketone was decreased and the formation of the unsaturated alcohols were increased comparing with nonfluorinated alcohols.[10]

Experimental

Reagents and catalysts were commercial products and were



Scheme 2.

used without purification. The ^{19}F nmr data were obtained on Hitach R24 F with CF_3COOH as an external standard (δ 0.00). The ^1H nmr data were recorded on Varian EM 390 with TMS as an internal standard (δ 0.00).

1, 1, 1-Trifluoro-4-phenyl-3-butyn-2-ol (*1a*). Into a solution of phenylacetylene (4.08 g, 40 mmol) and dry ether (30 m*l*), *n*-butyllithium (27 m*l*, 1.5 *M* in hexane) was added slowly at −78° C. α,α,α-Trifluoroacetaldehyde (3.7 g, 38 mmol) was bubbled into the above mixture at that temperature. After 2 hrs of stirring at −78°C, the reaction mixture was allowed to warm to the room temperature and then the whole solution was poured into 2% HCl solution. A crude product was extracted with diethyl ether. After the ethereal solution was dried over magnesium sulfate, the solvent was removed. Distillation gave 1,1,1-trifluoro-4-phenyl-3-butyn-2-ol in 74% yield, bp 82 °C/1.8 mmHg.

^{19}F nmr ($CDCl_3$): δ0.3 (CF_3, *d*, J_{CF_3-CH}=6.6 Hz). ^1H nmr ($CDCl_3$): δ3.83(OH), 4.87 (CH, *q*), 7.37(Ar-H).

Anal. (%). Calcd for $C_{10}H_7OF_3$; C, 60. 01; H, 3.53. Found; C, 59.74; H, 3.86.

1, 1, 1-Trifluoro-3-octyn-2-ol (*1b*). Into a solution of *n*-butylacetylene (6.2 g, 76 mmol) and dry ether (50 m*l*), *n*-butyllithium (52 m*l*, 1.5 *M* in hexane) was added slowly at −78°C. α, α, α-Trifluoroacetaldehyde (7.0 g, 71 mmol) was bubbled into the above mixture at that temperature. After 2 hrs of stirring at −78° C, the reaction mixture was allowed to warm to the room temperature and then the whole solution was poured into 2% HCl solution. An oily material was extracted with diethyl ether. After the ethereal solution was dried over magnesium sulfate, the solvent was removed. Distillation gave 1, 1, 1-trifluoro-3-octyn-2-ol in 72% yield, by 83–85° C /21 mmHg.

^{19}F nmr ($CDCl_3$): δ2.3 (CF_3, *d*, J_{CF_3-CH}=5.6 Hz). ^1H nmr ($CDCl_3$): δ0.9, 1.50, 2.30 (9H), 3.70 (OH), 4.73 (CH).

Anal. (%). Calcd for $C_8H_{11}OF_3$; C, 53.33; H, 6.15. Found; C, 53.37; H, 6.39.

(Z)-1, 1,-Trifluoro-4-phenyl-3-buten-2-ol (*3a*). Into solution of iso-butyl magnesium chloride derived from iso-butyl chloride (2.34 g, 25 mmol) and magnesium (0.66 g, 27 mmol) in dry ether (30 ml) at 0° C, dichlorobis [π-cyclopentadienyl] titanium (0.14 g, 0.56 mmol) and then 1,1,1-trifluoro-4-phenyl-3-butyn-2-ol (2g, 10 mmol) were added slowly at 0° C. After 1 hr of stirring at that temperature, the reaction mixture was poured into 2% aq HCl and then oily material was extracted with diethyl ether. After removing the solvent, distillation gave (*Z*)-1, 1, 1-trifluoro-4-phenyl-3-buten-2-ol in a yield of 88 %, bp 78–80 °C/3 mmHg.

^{19}F nmr ($CDCl_3$): δ0.16 (CF_3, *d*, J_{CF_3-CH}=6.6 Hz). ^1H nmr ($CDCl_3$): δ4.10 (OH), 4.97(CH,*d,q*,$J_{CH-CH=}$=9.8Hz) 5.83(CH=,*d,d*,$J_{CH=CH(cis)}$=12 Hz), 7.0(=CH, *d*) 7.33 (Ar-H).

Anal. (%). Calcd for $C_{10}H_9OF_3C$, 59.41; H, 4.49 Found; C, 59.18; H, 4.72.

(Z)-1,1,1-Trifluoro-4-phenyl-3-penten-2-ol .(*5a*). Into a reaction mixture of iso-butyl magnesium chloride derived from iso-butyl chloride (3.74 g, 40 mmol) and magnesium (0.97 g, 40 mmol) in dry ether (40 ml) at 0° C, dichlorobis [π-cyclopentadienyl] titanium (0.22 g, 0.9 mmol) and 1, 1, 1-trifluoro-4-phenyl-3-butyn-2-ol (2 g, 10 mmol) were added at room temperature. After 4 hrs. of stirring at room temperature, the solvent was removed under reduced pressure for 30 min. Into the reaction vessel, dry tetrahydrofuran (20 m*l*) was added and then methyl iodide (12.7 g, 90 mmol) was also added slowly. After stirring overnight, the reaction mixture was poured into 2% aq HCl solution, and then oily material was extracted with diethyl ether. After removing the solvent, distillation gave (*Z*)-1,1,1-trifluoro-4-phenyl-3-penten-2-ol in a yield of 63 %, bp 84–86° C/2 mmHg.

^{19}F nmr (CDC_3): δ0.6 (CF_3, *d*, J_{CF_3-CH}=5.4 Hz). ^1H nmr ($CDCl_3$): δ2.17 (CH_3, *d*, $J_{CH_3-H(Cis)}$=1.68 Hz), 3.17 (OH), 4.47 (CH, *d, q*, $J_{CH-CH=}$=9.4 Hz) 5.67 (CH=, *d, J*), 7.43 (Ar-H) *Anal.* (%). Calcd for $C_{11}H_{11}OF_3$; C, 61.11; H, 5.13. Found; C, 60.96; H, 4.99.

(Z)-1, 1, 1-Trifluoro-3-octen-2-ol (*3b*). 1, 1, 1-Trifluoro-3-octyn-2-ol (1.82 g, 10 mmol) was used in the above reaction, and after the worked up usually distillation gave (*Z*)-1, 1, 1-trifluoro-3-octen-2-ol in 85 % yield, bp 82–84° C/23 mmHg.

^{19}F nmr ($CDCl)_3$: δ0.8 (CF_3, *d*, J_{CF_3-CH}=6.6 Hz). ^1H nmr ($CDCl_3$): δ0.9, 1.40, 2.13 (9H), 3.97 (OH), 4.70 $J_{CH-CH=}$=10.5 Hz), 5.43 (CH=, *d, d*, $J_{CH-H(cis)}$=10.5 HZ), 5.83 (CH, *d, t*, J_{CH-CH_2}=7.5 Hz).

(Z)-1, 1, 1-Trifluoro-4-methyl-3-octen-2-ol (*5b*). 1, 1, 1-Trifluoro-3-octyn-2-ol (1.82 g, 10 mmol) and methyl iodide (12.7 g, 90 mmol) were used in the above reaction, and worked up similarly. Distillation gave (*Z*)-1, 1, 1-trifluoro-4-methyl-3-octen-2-ol in 62 % yield, bp 82–85 °C/21 mmHg.

^{19}F nmr ($CDCl_3$): δ0.8 (CF_3, *d*, J_{CF_3-CH}=6.6 Hz). ^1H nmr ($CDCl_3$): δ0.9, 1.40, 2.10 (9H), 1.80 (CH_3), 3.53 (OH), 4.7 (CH, *d, q*, $J_{CH-CH=}$=9.8 Hz), 5.30 (CH=, *d*).

Anal. (%). Calcd for $C_9H_{15}OF_3$; C, 55.09 H, 7.71 Found; C, 55.31; H, 7.86.

(E)-1, 1, 1-Trifluoro-4-iodo-4'-phenyl-3-buten-2-ol (*4a*). Into a reaction mixture of iso-butyl magnesium chloride derived from iso-butyl chloride (3.74 g, 40 mmol) and magnesium (0.97 g, 40 mmol) in dry ether (40 ml) at 0° C, dichlorobis [π-cyclopentadienyl] titanium (0.22 g, 0.9 mmol) and 1, 1, 1-trifluoro-4-phenyl-3-butyn-2-ol (2 g, 10 mmol) were added at room temperature. After 4 hrs stirring at room temperature, iodine (10.15 g, 40 mmol) in toluene (50 ml) was added slowly. After stirring overnight, the reaction mixture was poured into aq $Na_2S_2O_3$ solution, and then oily material was extracted with diethyl ether. After concentration, benzotrifluoride (0.73 g, 5 mmol) was added to that solution as internal standrad in order to calculate the yield. ^{19}F nmr yield of 4a was 45 %.

1, 1, 1-Trifluoro-3-buten-2-ol (*6*). A 100 m*l* 3-neck flask containing magnesium (1.26 g, 52 mmol), vinyl bromide (5.4 g, 50 mmol) and tetrahydrofuran (45 ml) was equipped with dry-ice condenser, thermometer and gas inlet tube. α, α, α-trifluoroacetaldehyde (2.94 g, 30 mmol) was bubbled into the flask under the ultrasonic irradiation. After 3 hrs of irradiation, the reaction mixture was poured into 2% aq. HCl solution, and then an oily material was extracted with diethyl ether. Distillation gave 1, 1, 1-trifluoro-3-buten-2-ol in 70%

yield, bp 99–100 °C.

^{19}F nmr ($CDCl_3$): δ2.0 (CF, d, J_{CF_3-CH}=5.6 Hz). ^{1}H nmr ($CDCl_3$): δ4.43 (CH, q), 4.67 (OH), 5.33–6.10 (CH=CH_2).

Phenylation of 1, 1, 1-Trifluoro-3-buten-2-ol. A mixture of 1, 1, 1-trifluoro-3-buten-2-ol (1.26 g, 10 mmol), iodobenzene (2.04 g, 10 mmol), triethylamine (1. 313 g, 13 mmol), 3.3 m*l* of acetonitrile and palladium acetate (0.0067 g, 0.03 mmol) was refluxed for 10 hrs under nitrogen atmosphere. The reaction mixture was cooled to 20° C, diluted with 30 m*l* of water and extracted with diethyl ether. The ether layer was washed three times with water, then dried over sodium sulfate. Solvent removal and distillation gave 1.1 g of 1, 1, 1-trifluoro-4-phenyl-2-butanone (8, bp 57–59° C/2 mmHg) and 0.62 g of (E)-1,1,1-trifluoro-4-phenyl-3-buten-2-ol (7, bp 76–77° C/1 mmHg). The total yield of phenylation was 85%.

1, 1, 1-Trifluoro-4-phenyl-2-butanone (8): ^{19}F nmr (CDC_3): δ0.83 (CF_3, s). ^{1}H nmr ($CDCl_3$): δ3.0 (−CH_2CH_2−, s), 7.3 (Ar-H)

(*E*)-1,1,1-Trifluoro-4-phenyl-3-buten-2-ol (7): ^{19}F nmr ($CDCl_3$): δ0.5 (CF_3, *d*, J_{CF_3-CH}=6 Hz). ^{1}H nmr (CDC l): δ2.98 (OH), 4.57 (CH, *d*, *1*, $J_{CH-CH=}$=7.2 Hz), 6.16 (CH=, *d*,*d*,$J_{CH=CH(trans)}$=16.5 Hz), 6.83(=CH, d), 7.36(Ar-H).

1, 1, 1-Trifluoro-4-penten-2-ol (*9*). A 100 ml 4-neck flask containing zinc powder (1.50 g, 23 mmol), manganese chloride (2.90 g, 23 mmol) and tetrahydrofuran (30 m*l*) was equipped with dry-ice condenser, thermometer, gas inlet tube and dropping funnel. After ultrasonic irradiation for 10 min, allyl bromide (2.30 g, 20 mmol) was added slowly and α, α, α-trifluoroacetaldehyde (1.96 g, 20 mmol) was bubbled into the above flask under the ultrasonic irradiation. After irradiating for 2 hrs, the reaction mixture was poured into 2% aq HCl solution and worked up as described previously. Distillation gave 1, 1, 1-trifluoro-4-penten-2-ol in a yield of 80 %, bp 100–101 °C

^{19}F nmr ($CDCl_3$): δ2.0 (CF_3, *d*). ^{1}H nmr ($CDCl_3$): δ2.43 (CH_2), 3.9 (CH), 4.1 (OH), 5.16 (=CH_2), 5.73 (CH=)

Phenylation of 1,1,1-Trifluoro-4-penten-2-ol. 1,1,1-Trifluoro-4-penten-2-ol (1.39 g, 10 mmol) was used in the above phenylation, and worked up as discribed previously. Distillation gave only one product, (*E*)-1,1,1-trifluoro-5-phenyl-4-buten-2-ol (10), in 80 % yield, bp 92°C/2 mmHg.

^{19}H nmr ($CDCl_3$): δ1.16 (CF_3, *d*) ^{1}H nmr ($CDCl_3$): δ2.5 (CH_2, *d*, *d*), 3.34 (OH), 3.9 (CH, *t*, *q*), 6.13 (CH=, *d*, *t*, $J_{CH=CH(trans)}$=15.7 Hz, $J_{CH_2-CH=}$=7.5 Hz), 6.50 (=CH, *d*, $J_{CH=CH}$=15.7 Hz), 7.14 (Ar-H).

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Arrhenius Parameters for the Thermal Decomposition of Trichloroethylene

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A thermal decomposition of trichloroethylene was studied in the temperature range of 440~460°C by using the conventional static system. In order to investigate the pressure dependence of reaction and to eliminate free radical process, propylene was used as the bath gas. The pressure range investigated was 10~900 Torr. The decomposition was the unimolecular dehydrochlorination and the reaction products were hydrogen chloride and dichloroacetylene.

Results were interpreted in terms of the Ric-Ramsperger-Kassel-Marcus (RRKM) unimolecular rate theory and the Arrhenius parameters were determined from fall-off behaviors. The Arrhenius parameters are found to be log A=13.8±0.2 sec^{-1} and E=56.6±0.7 kcal/mole, respectively.