brucination cycle applied to the +90.2° material gave 900 mg of volatiles (α_{365} +68.9°) and from the brucine 340 mg (α_{365} +122.1°) of volatiles. A gas chromatographic analysis of this last fraction gave 95.3% 2,3-dibromobutane, 2.5% 2-bromo-2-butene, 0.6% diethyl ether, and 1.5% $CFCl_3$. Differential scanning calorimetry applied to this best fraction indicated the dextrorotatory component was 70% of this mixture, the remainder being *d,l* and the other listed contaminants.

Registry No. (*R*,R**)-(±)-2,3-Dibromobutane, 598-71-0; brucine, 357-57-3; 2-bromo-2-butene, 13294-71-8; (*S,S*)-(−)-2,3-dibromobutane, 49623-63-4; (*R,R*)-(+)-2,3-dibromobutane, 58560-19-3.

Cu(I)-Catalyzed Coupling Reaction between Phenylmagnesium Bromide and 3,3,3-Trifluoropropene

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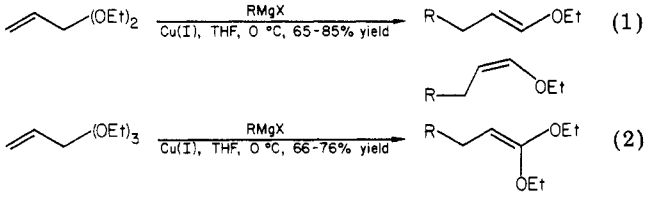
Allylic acetates,[1] ethers,[2] phosphates,[3] sulfones,[4] sulfides,[5] and sulfonium salts react with Grignard reagents (RMgX) in the presence of a catalytic quantity of Cu(I) with replacement of the heteroatom leaving group by R (from RMgX) via both S_N2 and S_N2' pathways. The S_N2/S_N2' ratio depends both on the substitution pattern of the allylic substrate and the leaving group. However, with α-ethylenic acetals, e.g., 3,3-diethoxypropene, and vinylic ortho esters, e.g., 3,3,3-triethoxypropene, substitution occurs with complete selectivity as outlined in eq 1[6] and 2.[7]



On the basis of these results we envisaged a copper-catalyzed coupling reaction between Grignard reagents and either 3,3-difluoropropene to give 1-fluoro-1-alkenes or 3,3,3-trifluoropropene to give 1,1-difluoro-1-alkenes. Since 3,3,3-trifluoropropene is readily available and relatively inexpensive, we first examined its reaction with simple Grignard reagents. Initial studies with *n*-butylmagnesium bromide were not promising as a complex mixture of products, none of which had the expected volatility for a C_7 molecule, was obtained. With phenylmagnesium bromide and 5% CuBr in THF at −6 °C, a mixture of products was obtained but in sufficiently high yield to facilitate isolation and characterization. At a 1:1 ratio of PhMgBr to alkene, GLC analysis indicated four principle components and one minor component in approximate relative yield of 21% (**1**), 20% (**2**), 2% (**3**), 26% (**4**), and 31% (**5**) (order of GLC elution). When the ratio of PhMgBr to olefin was increased to 2:1, the yields of the two more slowly eluting components fell (**4** and **5**), while the third component (**3**) now amounted to 10% of the products. The occurrence of **3** in significantly higher proportion corresponded with the appearance of a deep wine red color in the reaction mixture prior to quenching with aqueous NH_4Cl or Me_3SiCl.

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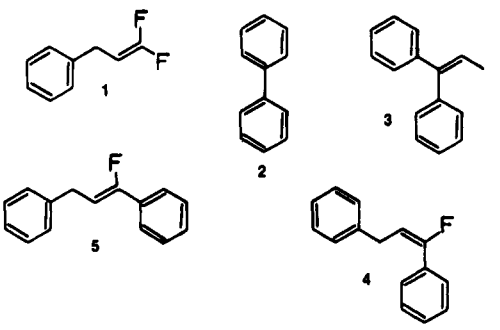
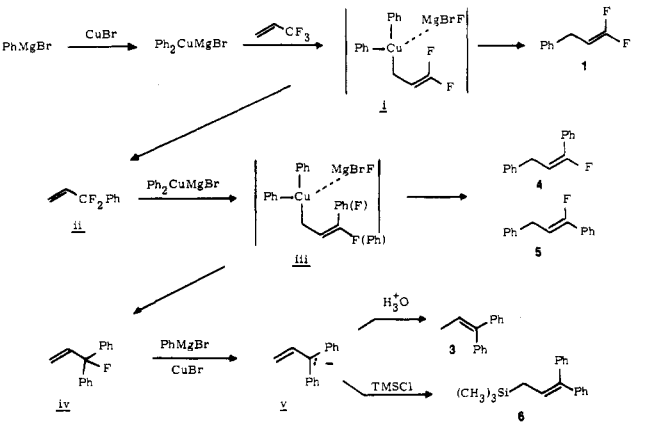
Chart I



Scheme I



The products were separated and purified by preparative GLC and characterized by ^1H NMR and mass spectrometry. All are known compounds[8,9] and were identified unambiguously as structures **1**–**5** (Chart I).

In analogy to the Cu(I)-catalyzed reaction of Grignard reagents with vinylic ortho esters, we expected the principal product to be 1,1-difluoro-3-phenyl-1-propene (**1**). Phenyllithium adds in good yield to 3,3,3-trifluoropropene (1:1 ratio) to give **1** with no evidence of **3**, **4**, or **5**.[8] However, when **1** is treated with a second equivalent of phenyllithium, addition occurs at C-1 followed by elimination of fluoride to give a mixture of (*E*)-1-fluoro-1,3-diphenylpropene (**4**) and (*Z*)-1-fluoro-1,3-diphenylpropene (**5**).[8] A third equivalent of phenyllithium effects the elimination of HF to give 1,3-diphenylpropyne.

In comparison, phenylmagnesium bromide does not react with 3,3,3-trifluoropropene in the absence of Cu(I). Nor as we discovered do **4** and **5** result from reaction of phenylmagnesium bromide with 1,1-difluoro-3-phenylpropene (**1**) in either the absence or presence of Cu(I) (THF, −6 °C). Compounds **4** and **5** must be formed by an alternate pathway for which **1** is not an intermediate. On

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0022-3263/83/1948-1902$01.50/0

the basis of the coincidence of the wine-red color and the product 1,1-diphenylpropene (3), we speculated that carbanion v must be an intermediate (Scheme I). This was established by quenching the reaction mixture with trimethylchlorosilane, which gave 1,1-diphenyl-3-(trimethylsilyl)propene (6, Scheme I). The mechanism is a matter for speculation since it remains to be established whether addition of organocuprates to olefins (especially unsaturated ketones) occurs by an electron-transfer mechanism[10] or by a nucleophilic addition mechanism,[11] or whether a Cu(III) adduct such as i is an intermediate. If i were an intermediate, the observed results could be readily explained. Transfer of a phenyl group from Cu to C-3 of the 1,1-difluoropropene moiety would give 1 while transfer to C-1 would give 3,3-difluoro-3-phenylpropene (ii). As an allylic fluoride ii would be susceptible to coupling with $Ph_2CuMgBr$ to give iii, which in analogy to i could transfer a phenyl group to either of two carbons, leading to a mixture of 4 and 5 or 3-fluoro-3,3-diphenylpropene (iv). The mechanism by which iv is transformed to v is unknown but must involve a reduction, possibly coupled with simultaneous Cu(I)-catalyzed linkage of PhMgBr to give biphenyl.

Obviously the copper-catalyzed coupling reaction of Grignard reagents with 3,3,3-trifluoropropene is not a very synthetically useful reaction, but these studies do establish the nature of the coupling and point to the feasibility of related reactions between other allylic fluorides for which regioselectivity may be less of a problem.

Experimental Section

3,3,3-Trifluoropropene was purchased from PCR Research Chemicals, Inc., and used without further purification. Tetrahydrofuran was dried and purified immediately prior to use by distillation over sodium metal. ^1H NMR spectra were obtained on a Model PS100 100-MHz FT NMR spectrometer. Tetramethylsilane was used as the internal standard. High-resolution electron-impact mass spectra were obtained on a modified Kratos/AEI MS90 mass spectrometer, operating at a dynamic resolution of M/ΔM 10 000. Low-resolution mass spectra were obtained with a consolidated 12-1108 mass spectrometer.

GC analysis and preparative GC were performed with a Hewlett-Packard 5710A gas chromatograph and a 12 ft × 0.25 in. 10% SE-30 on Gas-Chrom Q column.

Reaction of PhMgBr with CH_2=$CHCF_3$. A solution of phenylmagnesium bromide in THF (50 mL) was prepared by combining bromobenzene (4.26 mL, 0.0404 mol) and magnesium turnings (0.936 g, 0.0385 mol). The solution was cooled to −6 °C and dry CuBr (0.276 g, 1.93 mmol) added. A solution of CH_2=$CHCF_3$ (3.7 g, 0.0385 mol) in 50 mL of THF was slowly added over a period of 45 min. The reaction mixture was then allowed to warm to room temperature and after 5.5 h worked up by quenching with saturated aqueous NH_4Cl and extracting with pentane. The pentane extracts were dried over $MgSO_4$, filtered, and the product mixture (2.6 g) obtained by evaporation of the solvent. A typical GLC analysis on the SE-30 column programmed from 100–270 °C at 8°/min gave the following retention times: 1, 5.4 min; 2, 13.6 min; 3, 17.0 min; 4, 18.3; and 5, 19.3 min. The structure of 1 was confirmed by GLC comparison of a sample of 1,1-difluoro-3-phenylpropene prepared by the method of Fontanelli and Sianesi, and 2 by comparison to an authentic sample of biphenyl. Structures of all of the products were confirmed by ^1H NMR and mass spectrometry.

1,1-Difluoro-3-phenylpropene (1): ^1H NMR (CCl_4) δ 3.10 (d, 2 H, J = 8 Hz), 4.15 (m, 1 H), 7.00 (br s, 5 H); mass spectrum (high resolution) calcd m/e for $C_9H_8F_2$, 154.0594; found m/e, 154.0594; mass spectrum (low resolution), m/e (rel intensity) 154 (100), 153 (45), 134 (35), 133 (61), 127 (16), 104 (28), 103 (13), 91 (14), 78 (12), 77 (26), 51 (29).

1,1-Diphenylpropene (3): ^1H NMR (CCl_4) δ 1.72 (d, 3 H, J = 8 Hz), 6.12 (t, 1 H, J = 8 Hz), 7.18 (m, 10 H); mass spectrum (high resolution) calcd m/e for $C_{15}H_{14}$, 194.1096, found m/e, 194.1087; mass spectrum (low resolution), m/e (rel intensity) 195 (16), 194 (100), 193 (58), 192 (11), 191 (10), 179 (35), 178 (37), 165 (32), 152 (11), 147 (10), 117 (21), 116 (32), 115 (67), 105 (20), 103 (10), 91 (25), 89 (11), 77 (19), 51 (12).

(*E*)-1-Fluoro-1,3-diphenylpropene (4): ^1H NMR (CCl_4) δ 3.55 (d, 2 H, J = 8 Hz), 5.6 (dt, 1 H, $J_{H-F_{cis}}$ = 22 Hz, J_{H-H} = 8 Hz), 7.20 (m, 10 H); mass spectrum (high resolution) calcd m/e for $C_{15}H_{13}F$, 212.1002, found m/e, 212.1002; mass spectrum (low resolution), m/e (rel intensity) 213 (17), 212 (100), 211 (37), 197 (23), 196 (12), 192 (24), 191 (25), 189 (10), 165 (11), 135 (20), 134 (34), 133 (68), 115 (27), 109 (22), 103 (11), 91 (14), 77 (11).

(*Z*)-1-Fluoro-1,3-diphenylpropene (5): ^1H NMR (CCl_4) δ 3.55 (d, 2 H, J = 8 Hz), 5.45 (dt, 1 H, $J_{H-F_{trans}}$ = 36 Hz, J_{H-H} = 8 Hz), 7.18 (m, 10 H); mass spectrum (high resolution) calcd m/e for $C_{15}H_{13}F$, 212.1002, found m/e, 212.0997; mass spectrum (low resolution) was essentially identical to that of 4.

1,1-Diphenyl-3-(trimethylsilyl)propene (6): ^1H NMR (CCl_4) δ 0.08 (s, 9 H), 170 (d, 2 H, J = 8 Hz), 6.10 (t, 1 H, J = 8 Hz), 7.15 (m, 10 H); mass spectrum (high resolution) calcd m/e for $C_{18}H_{22}Si$, 266.1492, found m/e, 266.1491; mass spectrum (low resolution), m/e (rel intensity) 266 (32), 115 (13), 74 (15), 73 (100), 45 (15).

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Registry No. 1, 4980-68-1; 3, 778-66-5; 4, 85371-02-4; 5, 85371-03-5; 6, 83438-57-7; CuBr, 7787-70-4; phenyl bromide, 108-86-1; 3,3,3-trifluoropropene, 677-21-4.

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Acetoxycrenulide, a New Bicyclic Cyclopropane-Containing Diterpenoid from the Brown Seaweed *Dictyota crenulata*

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The small brown seaweeds (Phaeophyta) of the family Dictyotaceae are conspicuous members of most highly competitive tropical and subtropical habitats. Chemical studies have shown that these algae produce a variety of unique secondary metabolites that perhaps function as defensive compounds in the natural habitat.[1] In our studies of this algal group from the Gulf of California, Mexico, we have encountered several *Dictyota* species that produce new diterpenoid ring systems.[2,3] In this note we amplify upon our earlier work by reporting, in full, the structure of a new diterpenoid, acetoxycrenulide (1), which is a major metabolite, along with pachydictyol A,[4] of *D. crenulata* J. Agardh.[5] Acetoxycrenulide possesses a reg-

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