Portions of the filtrate were treated with methanol and pyridine and with sodium methoxide in methanol ass described in the general procedure. Absorptions in the NMR spectrum of a sample from the former procedure show only methyl α-chlorodiphenylacetate (outside of the phenyl region) while those of a sample from the latter procedure show only a mixture of methyl α-chlorodiphenylacetate and methyl α-methoxydiphenylacetate.

Treatment of Diaryl Ketones with Phenyl(bromodichloromethyl)mercury in the Presence of Dimethyl Acetylenedicarboxylate. A mixture of phenyl(bromodichloromethyl)mercury (2.0 g, 4.59 mmol), dimethyl acetylenedicarboxylate (1.9 g, 13.4 mmol), diaryl ketone (13.4 mmol), and dry benzene (15 mL) was heated at 80 °C under argon for 15–19 h. The progress of the reaction was monitored by TLC (ethyl acetate/hexane, 1:39) and GC (25-m OV-101 capillary). The reaction mixture was filtered through sintered glass (positive argon pressure), and the collected phenylmercuric bromide was washed with benzene. The benzene washings and filtrate were combined and examined by capillary GC.

The products from benzophenone were shown to be dichlorodiphenylmethane and α-chlorodiphenylacetyl chloride (area ratio 1:3) by careful comparison of capillary GC retention times with authentic samples. Treatment of the product mixture with dry methanol for 30 min at 25 °C converted the acid chloride to methyl α-chlorodiphenylacetate.

The products from fluorenone were shown to be 9,9-dichlorofluorene (very small amount) and 9-chlorofluorene-9-carbonyl chloride by careful comparison of capillary GC retention times with authentic samples.

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Registry No. 2, 119-61-9; 3, 486-25-9; 4, 3294-58-4; 5, 2051-90-3; 6, 2902-98-9; 7, 2235-01-0; 8, 51552-62-6; 9, 54311-64-7; 10, 85422-07-7; 16, 25023-01-2; 17, 5101-06-4.

Notes

Resolution of *d,l*-2,3-Dibromobutane by Entrapment in Brucine Crystals. Refutation of a Contrary Report

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Resolution of racemates of compounds lacking reactive functional groups (hydrocarbons, alkyl halides, etc.) has been difficult. We mentioned briefly in 1973 that the resolution of *d,l*-2,3-dibromobutane into both dextro- and levorotatory components could be effected with brucine since the dextrorotatory component was incorporated into the suspended solid brucine.[1] Since then we have learned from Professor S. Wilen[2] that he has used this method to obtain (+) and (−) fractions from a number of bromochlorofluoralkanes. As the original report is buried in a footnote to other work and as Chemical Abstracts searches failed to bring the method to light, we would like to call attention to this procedure by providing further confirmation. This has become important since contrary claims have been published:[4] "In our hands, contrary to these interesting claims, only *trans*-2-bromo-2-butene, the elimination product, and the active (−)-2,3-dibromobutane could be obtained from either the distillation or the brucine trapped material."

Winstein and Lucas[3] had applied brucine to *d,l*-2,3-dibromobutane to effect a kinetic resolution through destruction of the dextrorotatory component, presumably by dehydrohalogenation, leading to a sample with $[\alpha]_D$ −2.5°. There are numerous analogous examples in the literature employing this method, preferential destruction of one enantiomer. The method we describe has resulted in separation of both (+) and (−) samples, the former with $[\alpha]^{20}_D$ +26.4° (>70% of the maximum value). Isolation of both enantiomers as well as a high mass balance makes clear the fact (confirmed by the findings of Wilen) that interaction of alkyl halides with brucine is not a kinetic resolution by asymmetric destruction but rather is a preferential entrapment of one enantiomer.

This method is equally effective in resolving the antipodes of the *erythro*- and *threo*-2-bromo-3-chlorobutanes.[1]

Tanner and co-workers reported[4] a failure to reproduce these findings. However, a reading of their experiments indicates reaction times of 48, 70, 76 and 112 h instead of the 3 h we employed, resulting in a duplication of the earlier reported results of Lucas et al., which produced only (−)-2,3-dibromobutane and 2-bromo-2-butene.

Thus, with short reaction times resolution by preferential entrapment in the brucine crystals is the resolving process; with long contact times preferential dehydrohalogenation of dextrorotatory component occurs.[3,4]

Experimental Section

A slurry of brucine and *d,l*-2,3-dibromobutane (0.5:1.0 molar ratio) was agitated for 3 h at room temperature, after which the volatiles were removed by high-vacuum pumping to yield a levorotatory fraction. The solid residue was treated with aqueous acid and extracted to recover the dextrorotatory fraction. From 28.7 g of *d,l* dibromide there were recovered the following amounts of volatiles: 18.7 g, α_{365} −23.6°; 7.4 g, α_{365} +48.7°. This procedure was applied again with good effect to the dextrorotatory fraction, yielding 4.0 g of volatile fractions (α_{365} +18.8°) and 1.8 g of volatile fractions on acid release from the solids (α_{365} +90.2°). A third

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(2) Private communication: Prof. S. Wilen, The City College of The City University of New York, New York, NY 10031.

(3) Winstein, S.; Lucas, H. J. *J. Am. Chem. Soc.* **1939**, *61*, 1576, 2843. See also: Lucas, H. J.; Gould, C. W. *Ibid.* **1942**, *64*, 601. Winstein, S.; Buckles, R. E. *Ibid.* **1942**, *64*, 2780.

(4) Tanner, D. D.; Blackburn, E. V.; Kosugi, Y.; Ruo, T. C. S. *J. Am. Chem. Soc.* **1977**, *99*, 2722.

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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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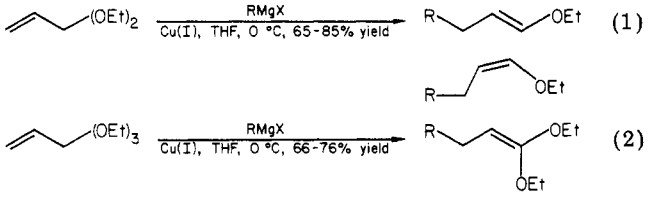
Allylic acetates,[1] ethers,[2] phosphates,[3] sulfones,[4] sulfides,[5] and sulfonium salts react with Grignard reagents (RMgX) in the presence of a catalytic quantity of Cu(I) with replacement of the heteroatom leaving group by R (from RMgX) via both S_N2 and S_N2' pathways. The S_N2/S_N2' ratio depends 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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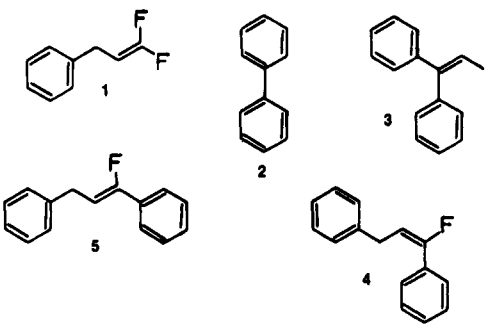
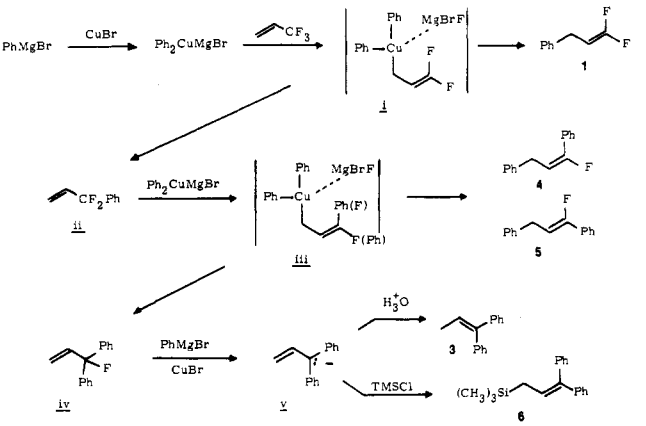
Chart I



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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