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ORGANOALUMINUM-INDUCED ADDITION OF POLYHALOMETHANE TO OLEFINS

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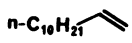
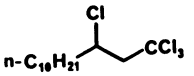
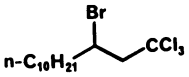
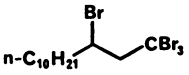
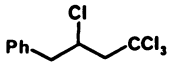
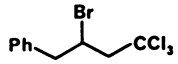
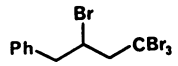
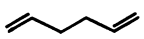
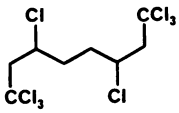
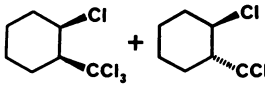
A mild procedure for the trimethylaluminum-induced addition of polyhalomethane to olefins has been described.

Despite the use of polyhalomethane (e.g. methylene chloride, chloroform, etc.) as a solvent for organoaluminum reagents, explosive reactions have been sometimes observed for mixtures of carbon tetrachloride with trialkylaluminums, alkylaluminum hydrides, and alkylaluminum halides.[1] The reactions appear to take the free-radical chain process involving the trichloromethyl radical as an initiator.[2] Although the risk is diminished when the carbon tetrachloride is in excess, such polyhalomethane are still regarded as dangerous solvents for organoaluminum compounds. However, by manipulating the hitherto uncontrolled reactivity of organoaluminum compounds-polyhalomethane systems,[3] we have successfully developed a new procedure for the regioselective addition of polyhalomethane to olefins as illustrated below.[4]

Reaction of 1-dodecene with polyhalomethane such as carbon tetrachloride, bromotrichloromethane, and carbon tetrabromide in the presence of trimethylaluminum under mild conditions gave rise to the corresponding adduct with rigorous regiospecificity in good to excellent yields. Some examples are listed in Table 1. A variety of trialkylaluminums were examined as initiators for the addition reaction. Among these only trimethylaluminum was found to be efficient. The reaction can be accelerated by the use of catalytic $Pd(PPh_3)_4$ (entries 6, 11, and 13).[5] Unfortunately, this reaction is not stereoselective. Attempted reaction of carbon tetrachloride with cyclohexene resulted in formation of a mixture of cis and trans isomers in a ratio of 1:1 (entries 12 and 13).[6]

Table 1. Addition of Polyhalomethane to Olefins in the presence of Me_3Al [a)]

Entry	Olefin	Polyhalomethane[b)]	Initiator (equiv.)	Solvent (temp, time)	Product	Yield/%[c)]
1		CCl_4	Me_3Al (4)	CCl_4 (RT, 15 h)		86
2		CCl_4	Me_3Al (2)	CCl_4 (RT, 15 h)		83
3		$BrCCl_3$	Me_3Al (4)	Hexane (RT, 4 h)		95
4		CBr_4	Me_3Al (4)	Hexane (RT, 4 h)		94
5		CCl_4	Me_3Al (4)	CCl_4 (RT, 20 h)		30
6		CCl_4	Me_3Al (4)/ $Pd(PPh_3)_4$ (0.05)	CCl_4 (RT, 15 h)		57
7		$BrCCl_3$	Me_3Al (4)	Hexane (RT, 2 d)		51
8		CBr_4	Me_3Al (4)	Hexane (RT, 1 d)		72
9		CBr_4	Me_3Al (4)	CH_2Cl_2 (RT, 1 d)		73
10		CCl_4	Me_3Al (4)	CCl_4 (RT, 2 d)		34
11		CCl_4	Me_3Al (4)/ $Pd(PPh_3)_4$ (0.05)	CCl_4 (RT, 2 d)		80
12		CCl_4	Me_3Al (4)	CCl_4 (RT, 20 h)	 (1:1)	20[d)]
13		CCl_4	Me_3Al (4)/ $Pd(PPh_3)_4$ (0.05)	CCl_4 (RT, 19 h)		60[d)]

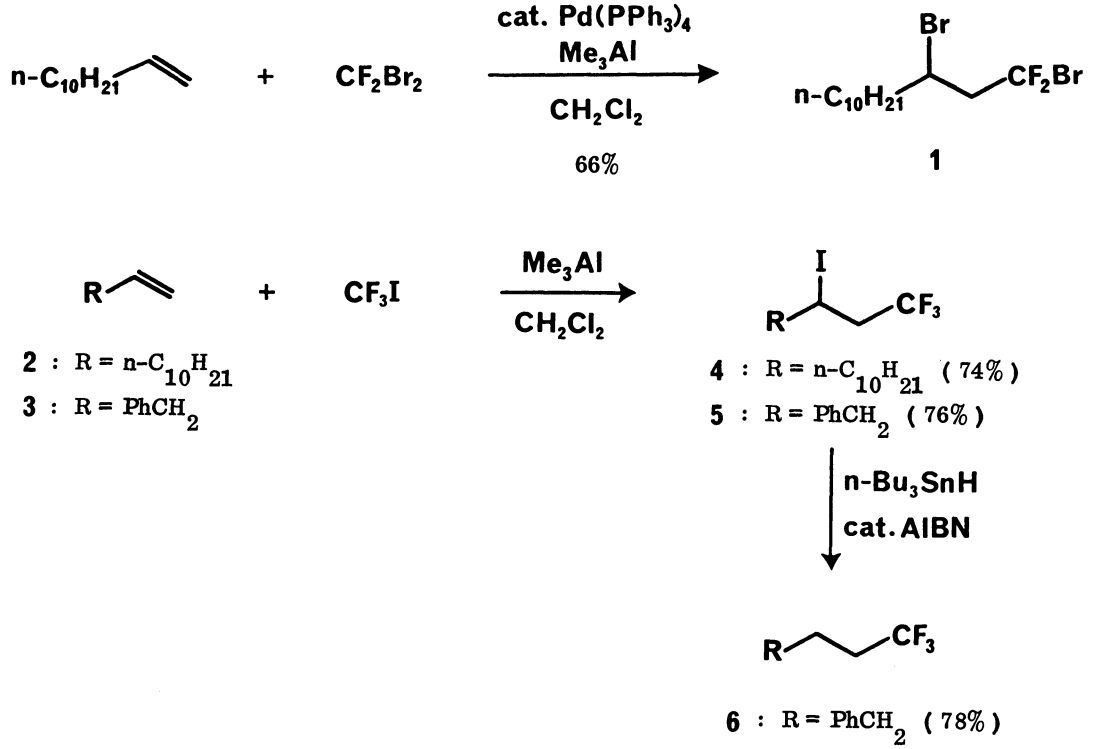
a) All reactions were carried out on a 1-mmol scale. The products were identified by comparison of the spectral properties with those of authentic samples.

b) Carbon tetrachloride was used as solvent. Except carbon tetrachloride, 4 equiv. of polyhalomethane was employed in hexane or CH_2Cl_2.

c) Isolated yield after column chromatography.

d) The isomeric ratio was determined by GC and ^1H NMR analysis. See Ref. 6.

The present organoaluminum-induced addition reaction has been applied to the polyfluoromethylation of olefins which is one of the most efficient and versatile methods for direct introduction of polyfluoromethyl group to organic molecules.[7] The addition of polyfluoromethane to olefins has been accomplished by photolysis, pyrolysis, electrolysis, free radical initiators, CuI-ethanolamine, or several transition-metal catalysts,[8] most of which required the troublesome sealed-tube experiments because of voratile polyfluoromethanes (e.g., bp -22.5 °C for iodotrifluoromethane). In sharp contrast to these existing procedures, our reaction proceeds under much milder conditions and yet guarantees satisfactory yields of addition products. For example, treatment of 1-dodecene with dibromodifluoromethane (4 equiv.) in the presence of trimethylaluminum (4 equiv.) and catalytic $Pd(PPh_3)_4$ (0.05 equiv.) at room temperature for 24 h produced the desired adduct **1** in 66% yield.[9] More significant is the observation of the remarkably facile addition of iodotrifluoromethane to olefins even at low temperature. Thus, exposure of olefin **2** and **3** with iodotrifluoromethane[10] (4 equiv.) and trimethylaluminum (1 equiv.) in methylene chloride at -25 °C for 8 h led to the corresponding adduct **4** and **5**, respectively, in 74-76% yields. Removal of the iodo moiety, if desired, has been effected with tributyltin hydride (1.2 equiv.) in benzene (50 °C, 30 min) in the presence of catalytic azobisisobutyronitrile (0.1 equiv.) as demonstrated by the conversion of **5** to 1,1,1-trifluoro-3-phenylpropane (**6**) in 78% yield.



The following experimental procedure may be illustrative. Gaseous iodotrifluoromethane[10] (4 mmol) was introduced and condensed in a 10-mL reaction flask at -78 °C under argon. To this were added successively methylene chloride (2 mL), 1-dodecene (1 mmol), and a 2 M hexane solution of trimethylaluminum (1 mmol) at -25 °C. The solution was maintained at -25°C for 8 h and poured into diluted HCl. The methylene chloride extracts were dried (Na_2SO_4) and evaporated. The residue was subjected to column chromatography on silica gel (hexane as eluant) to furnish the adduct **4** in 74% yield as a colorless oil.

While the range of iodopolyfluoroalkanes that could be used in this addition catalyzed by trimethylaluminum remains to be elucidated, the excellent success of trifluoromethylation combined with its potential versatility makes this method a highly useful one. Further work on examining the possible reactivity of iodotrifluoromethane to other functional units including acetylenes is currently in progress.

References

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2) H. Reinheckel, Tetrahedron Lett., 1964, 1939. See also Ref. 1.
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5) J. Tsuji, K. Sato, and H. Nagashima, Chem. Lett., 1981, 1169. The sole use of catalytic $Pd(PPh_3)_4$ in the absence of Me_3Al has resulted in total recovery of the starting olefins.
6) O. Gandolfi and M. Cais, J. Organometal. Chem., 125, 141 (1977).
7) M. Hudlicky, "Chemistry of Organofluorine Compounds," 2nd ed, Ellis, Horwood, Chichester, England (1976).
8) T. Fuchikami, Yuki Gosei Kagaku Kyokai Shi, 42, 775 (1984). See also: T. Fuchikami and I. Ojima, Tetrahedron Lett., 25, 303 (1984), and references cited therein.
9) P. Tarrant and A. M. Lovelace, J. Am. Chem. Soc., 76, 3466 (1954).
10) We appreciate Asahi Glass Co., Ltd. for a generous gift sample of iodotrifluoromethane.

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