Table I
Sulfinylamines Prepared by the Reaction of Primary Amines with 2 Mol Each of Butyllithium and Sulfur Dioxide

		RNSO			
Amine used (RNH_2)	Registry no.	Bp, °C (mm)	Yield, %	ν_{NSO}	Lit.
$C_6H_5NH_2$	62-53-3	55–60 (10)	46	1280, 1160	1
$2\text{-}MeC_6H_4NH_2$	95-53-4	83–85 (13)	59	1285, 1167	2
$4\text{-}MeC_6H_4NH_2$	106-49-0	75–80 (10)	58	1280, 1157	3
$2,6\text{-}Me_2C_6H_3NH_2$	87-62-7	97–100 (15)	52	1280, 1178	4
$2\text{-}MeOC_6H_4NH_2$	90-04-0	75–80 (0.2)	60	1286, 1156	2
$3\text{-}MeOC_6H_4NH_2$	536-90-3	66–72 (0.2)	50	1292, 1154	5
$4\text{-}MeOC_6H_4NH_2$	104-94-9	80–84 (0.5)	47	1305, 1157	6, 7
$4\text{-}ClC_6H_4NH_2$	106-47-8	100–105 (12)	45	1292, 1166	1
$n\text{-}C_3H_7NH_2$	107-10-8	80–90	30	1230, 1140	1
$n\text{-}C_4H_9NH_2$	109-73-9	80–90	20	1240, 1115	1
$c\text{-}C_6H_{11}NH_2$	108-91-8	55–60 (16)	14	1245, 1120	1

Experimental Section

All melting and boiling points were uncorrected. The ir and NMR spectra were determined with a Jasco Model IRA-1 spectrometer and a Hitachi Perkin-Elmer Model R-24 spectrometer, respectively. Solvents, amines, and sulfur dioxide were dried by common methods. Reactions were performed under dry nitrogen atmosphere. Identification of the products isolated was carried out by comparisons of boiling point, ir, and NMR spectra of authentic samples prepared by published methods.[1-9]

Standard Method for Preparation of *N*-Sulfinylamines. A. *N*-Sulfinyltoluidine. Under dry nitrogen atmosphere, *p*-toluidine (5.3 g, 50 mmol) was dissolved in dry tetrahydrofuran (50 ml) in a flask equipped with a mechanical stirrer, a condenser, a drying tube, a dropping funnel, and a nitrogen inlet, and treated with butyllithium (55 mmol in 40 ml of petroleum ether) at room temperature. After stirring for 30 min, sulfur dioxide gas was slowly introduced to the solution of *N*-lithiotoluidine (**1**, R = $p\text{-}CH_3C_6H_4$; δ 6.07, 6.47, dd, in tetrahydrofuran). Lithium *N*-tolylaminosulfinate (**2**, R = $p\text{-}CH_3C_6H_4$; δ 6.39, 6.59, dd) was formed exothermically. The muddy solution of **2** thus prepared in situ was treated again with butyllithium (55 mmol) with cooling to give a pale yellow suspension of lithium *N*-lithio-*N*-tolylaminosulfinate (**3**, R = $p\text{-}CH_3C_6H_4$; δ 6.66, br s). Sulfur dioxide (57 mmol) was allowed to react slowly with **3**, to give the reddish-orange solution of *N*-sulfinyltoluidine (**5**, R = $p\text{-}CH_3C_6H_4$), containing insoluble powders of lithium sulfite. The NMR spectrum of the solution was nearly the same as that of pure **5**. After refluxing for 2 hr, separation of insoluble materials by decantation method, and evaporation of solvent, the liquid layer was distilled in vacuo to afford *N*-sulfinyltoluidine: yield 3.2 g (40%); bp 85–90° (11 mm); ir (neat) ν_{NSO} 1280 and 1156 cm^{-1}. The ir and NMR spectra were in good agreement with those of the authentic sample prepared by the published method.[3] The solid mass obtained from the residue in the decantation or in the distillation showed the ir bands at 1010 and 960 cm^{-1} which were ascribable to $\nu_{SO_3^{2-}}$ bands of lithium sulfite.

Other aromatic *N*-sulfinylamines were also prepared and isolated in the same manner described above, and the structure of **5** obtained was identified by the comparison of ir and NMR spectra with those of authentic samples.[1-9]

In a separate experiment, the suspension of **2** or **3** (R = $p\text{-}CH_3C_6H_4$) was heated at 180° under reduced pressure (20 mm), but *N*-sulfinylamine (R = $p\text{-}CH_3C_6H_4$) was never obtained. The residue was hydrolyzed by dilute acid to recover toluidine in good yield (80–90%).

B. Aliphatic *N*-Sulfinylamines. Aliphatic *N*-sulfinylamines were prepared in the same procedure mentioned above. However, aliphatic *N*-sulfinylamine is readily hydrolyzed by moisture, so the suspension containing **5** and lithium salt in tetrahydrofuran was directly distilled in vacuo, and the distillate was trapped by cooling using liquid nitrogen. The distillate was fractionally redistilled to separate **5** (R = alkyl).

Equimolar Reaction of *N*-Lithio-2,6-xylidine with Sulfur Dioxide. Sulfur dioxide (50 mmol) was introduced slowly into the solution of *N*-lithio-2,6-xylidine (50 mmol) prepared in situ in tetrahydrofuran with cooling. The NMR and ir spectra of the reaction mixture coincided well with those of an equimolar mixture of free 2,6-xylidine (**6**) (multiplet at δ 6.2–6.8; ν_{NH_2} at 3380 and 3450 cm^{-1}) and *N*-sulfinyl-2,6-xylidine (**8**) (br singlet at δ 6.94; ν_{NSO} at 1280 and 1178 cm^{-1}). Isolation of *N*-sulfinylxylidine from the mixture failed by distillation.

Registry No.—**5** (R = Ph), 1122-83-4; **5** (R = $2\text{-}MeC_6H_4$), 15182-74-8; **5** (R = $4\text{-}MeC_6H_4$), 15795-42-3; **5** (R = $2,6\text{-}Me_2C_6H_4$), 17420-02-9; **5** (R = $2\text{-}MeOC_6H_4$), 17419-98-6; **5** (R = $3\text{-}MeOC_6H_4$), 17420-00-7; **5** (R = $4\text{-}MeOC_6H_4$), 13165-69-0; **5** (R = $4\text{-}ClC_6H_4$), 13165-68-9; **5** (R = C_3H_7), 53437-16-4; **5** (R = C_4H_9), 13165-70-3; **5** (R = $c\text{-}C_6H_{11}$), 30980-11-1.

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Solvolysis of Covalent Arylsulfonylmethyl Perchlorates. General Base Catalysis by Dipolar, Aprotic Solvents

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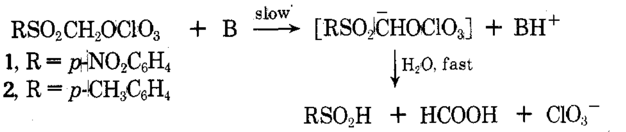
Dimethyl sulfoxide (Me_2SO) as well as the $Me_2SO\text{–}H_2O$ binary system are valuable reaction media for many organic reactions. The solvation properties of Me_2SO are characteristic of those of dipolar, aprotic (DPA) solvents and have been reviewed in detail.[1-3] In $Me_2SO\text{–}H_2O$ strong intermolecular interactions occur between the components and recent studies indicate that the behavior of these mixtures may be rationalized by assuming the formation of thermolabile, nonstoichiometric 1:2 complexes and by considering the effect of Me_2SO on the diffusionally averaged water structure.[4-6]

In this paper we focus our attention on the dynamic basicity (also referred to as "kinetic basicity") of Me_2SO and $Me_2SO\text{–}H_2O$ mixtures employing the rates of irreversible deprotonation of two carbon acids as a kinetic probe. The carbon acids are the covalent arylsulfonylmethyl perchlorates **1** and **2** which hydrolyze via a mechanism involving general base catalysis (Brönsted β ca. 0.5, primary kinetic



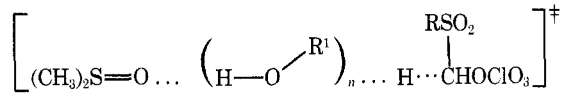
$$\mathrm{RSO_2CH_2OClO_3} + \mathrm{B} \xrightarrow{\text{slow}} [\mathrm{RSO_2\bar{C}HOClO_3}] + \mathrm{BH^+} \xrightarrow{\mathrm{H_2O},\ \text{fast}} \mathrm{RSO_2H} + \mathrm{HCOOH} + \mathrm{ClO_3^-}$$

1, R = *p*-$NO_2C_6H_4$
2, R = *p*-$CH_3C_6H_4$

deuterium isotope effect, k_H/k_D ca. 6).[7,8] Since **1** and **2** show a coveniently fast "water reaction" (B = H_2O), the rates of hydrolysis may serve as a specific probe for the dynamic basicity of aqueous and mixed aqueous solutions in the absence of other active Brönsted bases.[8]

In view of our earlier work[8] and results obtained by Hibbert and Long[9] for the rate-determining detritiation of tritiated malononitriles in Me_2SO-H_2O, it was anticipated that the initial addition of Me_2SO to water would cause a rate acceleration and that a kinetic maximum would be reached around the solvent composition for which a maximum in the diffusionally averaged water structure has been claimed (mole fraction of water, n_{H_2O}, ca. 0.7–0.8). This expectation was not borne out in practice. Instead, we observe a continuous and strong increase in rate upon the gradual addition of Me_2SO until at $n_{H_2O} = 0.62$ the rate becomes too fast to be measured with our kinetic equipment (Table I; rates relative to that in pure water are plotted as a function of n_{H_2O} in Figure 1). It may be noted that the pseudo-first-order rate constants (k_{obsd}) increase much more rapidly than a linear relationship with the Me_2SO concentration would require. The small change of the magnitude of the primary kinetic deuterium isotope effect (k_H/k_D) as a function of n_{H_2O} indicates that in the Me_2SO-rich mixtures the mechanism of hydrolysis does not change from a base-catalyzed process to nucleophilic substitution. Presumably, the increase in k_{obsd} may be attributed to general base catalysis by Me_2SO, most likely by stabilizing the transition state for water-catalyzed deprotonation.[10] A similar explanation may be advanced for the Me_2SO-catalyzed ethanolysis (Table I). A schematic representation of the transition state is depicted in Chart I, taking into account the known strong interaction between Me_2SO and hydrogen bonding donors like water and ethanol. Previously, Benoit and Lam[11] have demonstrated that H_3O^+ will be more strongly solvated by Me_2SO than by water. An additional factor that may contribute to transition state stabilization in Me_2SO-H_2O is the better solvation[1] of the charge dispersed transition state by Me_2SO than by H_2O.[12] In the highly aqueous mixtures ($n_{H_2O} > 0.8$) we cannot exclude the possibility that a rate-accelerating "water structure effect" is superimposed on the Me_2SO-catalyzed process,[13] but reliable experimental support for this effect is lacking.

Chart I



R¹ = H, C_2H_5

As shown in Table I, other dipolar, aprotic solvents like sulfolane (tetramethylene sulfone, TMS), *N,N*-dimethylformamide (DMF), and hexamethylphosphortriamide (HMPA) also exert rate-accelerating effects on the hydrolysis of **1** and/or **2**. The effect of the poor hydrogen bond acceptor TMS[14] is only modest. The relative efficiencies of Me_2SO, DMF, and HMPA as base catalysts are reasonably correlated with their hydrogen bonding acceptor abilities.[15]

It is difficult to establish the number of water molecules (n) present in the transition state viewed in Chart I, but the $\Delta S^{\ddagger}$ values for the H_2O-Me_2SO mixtures (Table I) are difficult to reconcile with $n > 2$. Since the decrease of the solvent deuterium isotope effect (k_{H_2O}/k_{D_2O}, Table I) upon increasing Me_2SO concentration could be indicative of solvolysis via a transition state for which $n = 0$, we have investigated the reaction of **1** with Me_2SO, DMF, and HMPA in an inert medium like anhydrous 1,4-dioxane (Table I).[16] Fairly rapid solvolysis occurs and the reaction products formed from **1** in dioxane–Me_2SO ($n_{Me_2SO} = 0.10$) are identical with those formed upon hydrolysis (see Experimental Section). The magnitude of the primary kinetic deuterium isotope effect (Table I) provides compelling evidence[17] for rate-determining deprotonation of the substrate. Highly efficient catalysis by traces of hydroxide ion[18] can be excluded because of the nearly identical rates of solvolysis in the presence of different concentrations of HCl or $HClO_4$. Catalysis by small amounts of water is also very unlikely, since addition of minor quantities of water (0.3–1.3 *M*) decreased rather than increased the rates of solvolysis of **1** in dioxane–Me_2SO ($n_{Me_2SO} = 0.10$). Consequently, we assume that **1** solvolyzes via rate-determining proton transfer to Me_2SO, DMF, and HMPA; approximate second-order rate constants are, respectively, $51 \times 10^{-3}\ M^{-1}\ sec^{-1}$ ($n_{Me_2SO} = 0.00–0.10$), $9.6 \times 10^{-3}\ M^{-1}\ sec^{-1}$ ($n_{DMF} = 0.00–0.10$), and $1130 \times 10^{-3}\ M^{-1}\ sec^{-1}$ ($n_{HMPA} = 0.00–0.05$). The superior hydrogen bonding capability of HMPA is again reflected in the high efficiency of this molecule as a general base.

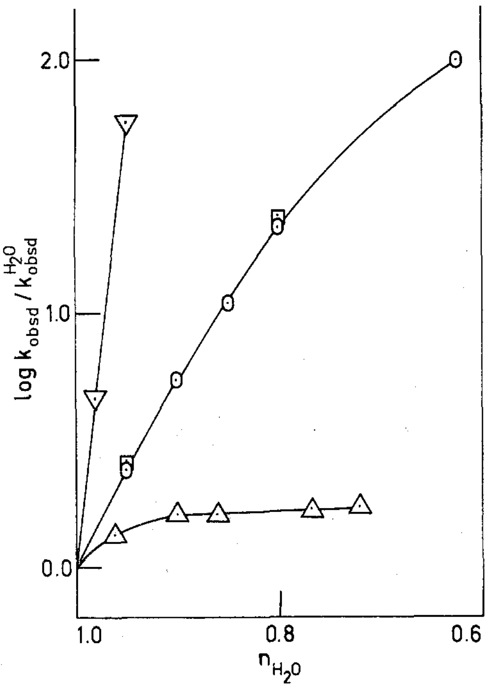


Figure 1. Relative rates of solvolysis of **1** and **2** vs. mole fraction of water: △, **2** in H_2O–TMS; ○, **1** in H_2O-Me_2SO; □, **2** in H_2O-Me_2SO; ▽, **1** in H_2O–HMPA.

The significantly greater dynamic basicities of Me_2SO, DMF, and HMPA as compared with water in the deprotonation of **1** and **2** in water as well as in dioxane as the solvent are noteworthy. Often, acids are less dissociated in Me_2SO and in Me_2SO-H_2O mixtures than in water, mainly owing to weaker solvation of the conjugate anions when the possibility of hydrogen bonding interaction is reduced.[19] Our results support Bordwell's recent conclusion[20] that in a particular medium kinetic acidities provide only a rough guide to carbanion stabilities. In the solvolysis of **1** and **2**, the transition state is reached early on the reaction coordinate (Brönsted β coefficient[7] ca. 0.5) and its free enthalpy most likely will be primarily dependent on the strength of the hydrogen bonding interaction between substrate and base which precedes proton transfer.[21] This sit-

Table I
Pseudo-First-Order Rate Constants (k_{obsd}), Activation Parameters, and Deuterium Isotope Effects for the Solvolysis of 1 and 2 in Different Solvents at 25°

Compd	Solvent	n_{H_2O}[a]	$k_{obsd} \times 10^3$, sec^{-1}	$\Delta H^‡$, kcal mol^{-1}	$\Delta S^‡$, eu	k_H/k_D[b]	k_{H_2O}/k_{D_2O}[c]
1	H_2O	1.000	3.25	18.4 ± 0.3	−8 ± 1	5.6	1.7
1	H_2O–Me_2SO	0.950	7.83	19.2 ± 0.3	−4 ± 1		
1	H_2O–Me_2SO	0.900	17.7	18.0 ± 0.3	−6 ± 1		
1	H_2O–Me_2SO	0.850	35.5	17.8 ± 0.3	−5 ± 1		
1	H_2O–Me_2SO	0.800	70.6	16.3 ± 0.3	−9 ± 1	6.3	1.3
1	H_2O–Me_2SO	0.625	322				1.1
1	H_2O–HMPA	0.980	15.1				
1	H_2O–HMPA	0.950	185				
1	H_2O–DMF	0.900	24.7				
1	H_2O–DMF	0.800	71.5				
1	EtOH	1.000[d]	4.51	15.8 ± 0.3	−16 ± 1		
1	EtOH–Me_2SO	0.900[d]	18.4				
1	Dioxane–Me_2SO	0.100[e]	62.8	12.8 ± 0.3	−21 ± 1	8.0	
1	Dioxane–HMPA	0.010[f]	13.0				
1	Dioxane–HMPA	0.030[f]	37.2				
1	Dioxane–HMPA	0.050[f]	67.0				
1	Dioxane–DMF	0.100[g]	11.5				
1	Dioxane–DMF	0.200[g]	29.0				
1	Dioxane–DMF	0.300[g]	53.8				
2	H_2O	1.000	0.605	19.7 ± 0.3	−7 ± 1		
2	H_2O–Me_2SO	0.950	1.58				
2	H_2O–Me_2SO	0.800	14.7				1.25
2	H_2O–DMS	0.950	0.688				
2	H_2O–TMS	0.960	0.814				
2	H_2O–TMS	0.900	0.967				
2	H_2O–TMS	0.860	0.965				
2	H_2O–TMS	0.768	1.01				
2	H_2O–TMS	0.720	1.04				

[a] Mole fraction of water. All solvent systems contained 10^{-3}–10^{-2} *N* HCl or $HClO_4$ to suppress catalysis by other bases than the solvent molecules. Me_2SO = dimethyl sulfoxide, HMPA = hexamethylphosphortriamide, DMF = *N,N*-dimethylformamide, DMS = dimethyl sulfone, TMS = tetramethylene sulfone (sulfolane). [b] Primary kinetic deuterium isotope effect. [c] Solvent deuterium isotope effect. [d] Mole fraction of EtOH. [e] Mole fraction of Me_2SO. [f] Mole fraction of HMPA. [g] Mole fraction of DMF.

uation may be contrasted with the deprotonation reaction of malononitriles,[9] for which the proton is transferred almost completely in the transition state (Brönsted β ca. 1.0). In this case the Brönsted basicity rather than the hydrogen bond basicity of the base will be the dominating factor. This will explain the sharp decrease of the rate of deprotonation in Me_2SO–H_2O mixtures below n_{H_2O} = 0.3 as found by Hibbert and Long.[9]

Experimental Section

Materials. The perchlorates 1 and 2 used in the kinetic experiments were analytically pure compounds which were prepared as described previously.[7] The water used in the kinetic measurements was demineralized and distilled twice in an all-quartz distillation unit. Deuterium oxide (99.75% D_2O) was obtained from Merck (uvasol quality) and was used as such. The organic solvents were obtained from Merck and were of the best grade available (water content below 0.1%). Dioxane was filtered through active, neutral alumina in a nitrogen atmosphere and stored under nitrogen at 0°. Solvent mixtures were usually made up by weight.

Product Analysis. The products formed upon complete solvolysis of 1 in dioxane–Me_2SO (n_{Me_2SO} = 0.10) were examined using spectroscopic techniques. The uv spectrum of the reaction mixture was identical with that of *p*-nitrobenzenesulfinic acid and differed significantly from that of the corresponding sulfonic acid. The formation of chloric acid was shown by a positive test with manganous sulfate and polyphosphoric acid.[22] The sharp peak at δ 8.5 ppm in the NMR spectrum of the reaction mixture revealed the formation of formic acid. After rate-determining deprotonation by Me_2SO, the final reaction products are most likely formed via rapid product-forming steps involving traces of water (< 0.1%) present in the solvent mixture.

Kinetic Measurements. Pseudo-first-order rate constants, k_{obsd}, were obtained using the uv technique described previously.[7,8] Solvolysis was accurately first order in all cases. Rate constants were reproducible to within 2%. The thermodynamic quantities of activation were calculated from k_{obsd} values at three to five temperatures between 25 and 45°.

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Registry No.—1, 26452-84-6; 2, 14894-56-5.

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Halogen Interchange in Alkyl Halides Using Molybdenum(V) Chloride[1a]

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The interconversion of haloalkane congeners by halide exchange (Finkelstein halide interchange) is a synthetically useful procedure when applied to primary and, to a lesser degree, secondary alkyl halides. Most frequently these interchanges involve the replacement of chloride or bromide with iodide, occur by an SN2 mechanism,[2] and are usually accomplished by treating the alkyl halide with sodium iodide in an appropriate solvent.[3] In general, the replacement of iodide by bromide or chloride, or of bromide by chloride, requires a large excess of the inorganic halide and elevated temperatures.[7,8] Alkyl fluorides do not undergo halide interchange under these conditions.[11,12]

We wish to report that alkyl iodides, bromides, and *fluorides* can be converted to alkyl chlorides in modest to good yields by reaction with molybdenum(V) chloride.

$$\mathrm{RX} \xrightarrow[\mathrm{CH_2Cl_2}]{\mathrm{MoCl_5}} \mathrm{RCl}$$

A summary of the results obtained on treatment of various representative substrates is given in Table I.

Several specific points related to the data in Table I deserve brief comment. First, this reaction sequence seems applicable to the conversion of secondary and tertiary alkyl fluorides, bromides, and iodides to the corresponding chloride. As suggested by the nearly quantitative recovery of 1-bromooctane, molybdenum(V) chloride does not affect halogen interchange in primary alkyl bromides. By comparison, 1-iodo- and 1-fluorooctane react readily. This dramatic difference in reactivities suggests the possibility of selective halogen interchange such as, for example, the conversion of a secondary alkyl bromide, iodide, or fluoride to the corresponding chloride in the presence of a primary alkyl bromide (cf. last entry in Table I).

Second, the conversion of 1-iodooctane to 1-chlorooctane is accompanied by the formation of some of the rearranged isomer, 2-chlorooctane. In contrast, the reaction of 1-fluorooctane occurs with extensive rearrangement.

Third, in a effort to probe the mechanism of halogen interchange we have examined the stereochemistry of the product produced by the reaction of molybdenum(V) chloride with (−)-(*R*)-2-bromooctane[13] (α^{20}_{589} −38.4°, 90% optical purity). The resulting 2-chlorooctane was completely racemic. It is, however, not possible to make a definitive statement concerning the stereochemistry of the carbon–chlorine bond-forming step, since under comparable conditions both optically active 2-chlorooctane[13] (α^{20}_{589} −30.7°, 97% optically pure) and optically active 2-bromooctane are completely racemized in less than 6 min.[14] One conceivable mechanism that accounts for these observations, as well as the 1,2 migrations observed with certain substrates, involves a Lewis acid assisted ionization of the carbon–halogen bond followed by conversion of this carbonium ion to chlorocarbon by reaction with a halometallo–ate complex.

Table I
Reaction of $MoCl_5$ with Various Alkyl Halides[a]

RX (concn, *M*)	Registry no.	Alkyl chloride	Registry no.	Yield,[b] % (recovered RX, %)
2-Fluoro-2-methylpropane[c] (2.0)	353-61-7	2-Chloro-2-methylpropane	507-20-0	49
2-Fluorooctane (2.0)	407-95-4	2-Chlorooctane	628-61-5	71
1-Fluorooctane[d] (4.5)	463-11-6	1-Chlorooctane	111-85-3	12
		2-Chlorooctane		58
2-Bromo-2-methylpropane (2.0)	507-19-7	2-Chloro-2-methylpropane		69
2-Bromooctane (2.0)	5978-55-2	2-Chlorooctane	51261-14-4	60
1-Bromooctane (1.0)	111-83-1	1-Chlorooctane		5 (94)
2-Iodo-2-methylpropane (1.5)	558-17-8	2-Chloro-2-methylpropane		48
2-Iodooctane (1.5)	557-36-8	2-Chlorooctane		67
1-Iodooctane (1.0)	629-27-6	1-Chlorooctane		66
		2-Chlorooctane		13
1-Iodo-2-phenylethane (1.5)	17376-04-4	1-Chloro-2-phenylethane	622-24-2	60
Fluorocyclohexane (3.0)	372-46-3	Chlorocyclohexane	542-18-7	62
Bromocyclohexane (2.0)	108-85-0	Chlorocyclohexane		60
1,1-Difluorocyclohexane (1.5)[e]	371-90-4	1,1-Dichlorocyclohexane	2108-92-1	31
1,3-Dibromobutane (2.0)	107-80-2	1-Bromo-3-chlorobutane	56481-42-6	61

[a] Unless otherwise indicated all reactions were carried out in CH_2Cl_2 solution at room temperature under an inert atmosphere of dry nitrogen. The concentration of molybdenum(V) chloride was ~1.0 *M*. [b] Yields were determined by quantitative vapor phase chromatography and are based on alkyl halide. [c] Carried out at −50°. [d] Performed at −78°. [e] Under similar conditions α,α,α-trifluorotoluene does not react with $MoCl_5$.