Preparation of Highly Reactive Metal Powders and Their Use in Organic and Organometallic Synthesis

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The reaction of organic and inorganic substrates at a metal surface, either in a catalytic fashion or in an oxidative addition reaction with consumption of the metal, represents an extremely important area of chemistry. Chemists have continually tried to increase the reactivity of the metal in order to allow known reactions to be carried out under milder conditions, to improve yields and save energy, or to extend the reaction to less reactive substrates. In recent years, several new approaches to this old problem have been found. We have developed a method for generating metal powders by the reduction of the metal salt with an alkali metal in an ethereal or hydrocarbon solvent.[1-12] The black metal powders generated by this procedure are frequently vastly superior to the commercial metal or standard activating techniques. Another approach which has received considerable attention is one that has evolved from Skell's carbon vapor reactor, namely the metal atom or metal vaporization technique.[13-25a] This approach utilizes the high chemical potential of metal atoms by co-condensing the metal vapor and the organic or inorganic substrate. Also, Klabunde has generated highly reactive metal slurries by co-condensing metals with various solvents.[24,25]

A major portion of this Account will be concerned with the generation of activated metals using the reduction procedure. One goal is to show how these new, highly reactive metals can be used to prepare new organic and organometallic compounds.

Generation of Activated Metals via the Reduction of Metal Salts

The reduction of metal salts from ethereal or hydrocarbon solvents, using alkali metals as reducing agents, leads to highly reactive metal powders.[1-12] The reduction is most conveniently carried out by using an alkali metal and a solvent with a boiling point which exceeds the melting point of the alkali metal. However, in some cases reducing agents such as lithium work. The metal salt to be reduced must also be partially soluble in the solvent, and the reductions should be carried out under an argon atmosphere. The reductions in most cases are exothermic, and in some cases very exothermic, and generally are complete within a few hours, producing a fine black powder of the metal. In addition, 1 or more mol of an alkali salt is also produced during the reduction, and it would seem from present data that a composite polycrystalline material is being generated. In addition to the above procedure, we have recently found that for certain metals the addition of simple alkali salts or Lewis bases before the reduction is carried out yields black metal powders of even higher reactivity.[3,4,26]

$$MX_n + nK \rightarrow M + nKX$$

The apparatus required is very simple. The reductions are usually carried out under argon in a three-neck flask equipped with condenser, septum, heating mantle, and magnetic stirring. In some cases, the metal salt to be reduced is dried overnight in a flask under vacuum, or else the anhydrous salt is added to the flask under argon. Freshly distilled, dry solvent is then added to the flask with a syringe. Finally, the alkali metal is added, and the resulting mixture is heated to the melting point of the alkali metal. For the higher boiling solvents, the reduction can usually be carried out below the boiling point of the solvents.

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For most of the chemistry discussed below, potassium (Baker purified) was used as the reducing agent. Very impure potassium or sodium generally led to much reduced reactivity of the activated metals. In most cases, the following reactions of the activated metals with organic and inorganic substrates were carried out in the vessel and solvent used for the reduction. In some cases, the solvent was stripped off, and a different solvent was added to carry out the reaction. The alkali salts generated in the reduction process are not removed prior to any additional chemistry, and in some cases it will be seen that they prove harmful to the desired reactions.

Even though we have had no trouble with fires or explosions caused by the activated metals, extreme caution in working with these materials should be exercised. Until a person becomes familiar with the characteristics of the metal powder involved, extreme caution should be taken at every step. To date every metal powder we have generated will not spontaneously ignite if removed from the reaction vessel wet with solvent. In spite of this, we would recommend that all metal powders be transferred under an argon atmosphere. If the metal powders are dried before being exposed to the air, some have been found to be pyrophoric, such as magnesium (generated via the KI procedure discussed below) and aluminum. The heat generated during the reduction process can be troublesome when the metal salts in question are very soluble in the solvents used. Reduction of $ZnCl_2$ in THF[2,11] and also $FeCl_3$ in THF[27] were both fairly exothermic, and extreme caution should be used at the start of the reduction of these and other very soluble salts. Use of sodium–potassium alloy as a reducing agent with these salts is not recommended, and can lead to explosive conditions.

Activated Magnesium

Grignard reagents represent one of the most important and versatile classes of organometallic intermediates known to the synthetic chemist. In spite of this, a vast number of Grignard reactions fail due to the unreactivity of the alkyl or aryl halide. Also, in some cases, coupling or eliminations plague the Grignard reaction.

Prior to our studies, there were three modifications of the general procedure for the direct synthesis of difficult-to-form Grignard reagents from the reaction of magnesium metal and an organic halide: (1) use of higher reaction temperatures, (2) use of a more strongly coordinating solvent,[28-32] and (3) activation of the magnesium metal.[33,34] The third method consists of activation of the magnesium by reduction of the size of the metal particle[35] or by a chemical reaction. The Gilman catalyst,[33] which involves the addition of iodine to activate the magnesium, is representative of this technique. Ethylene bromide or ethyl bromide has been employed in catalytic amounts to activate the magnesium surface and in molar quantities as an entrainer.[36] Certain transition metal halides have proven to be useful catalysts.[37a] Recently, Ashby combined the three techniques to prepare some alkylmagnesium fluorides.[34]

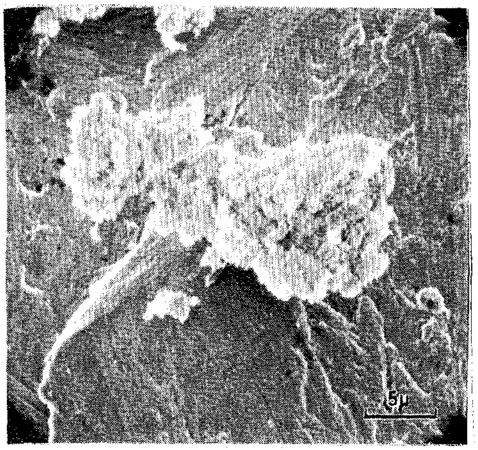

Figure 1. Activated magnesium prepared by potassium reduction of $MgCl_2$ in the presence of KI.

The conditions we have found most convenient for the preparation of the active magnesium involve the reduction of anhydrous $MgCl_2$ with potassium in refluxing THF.[3,4] The reduction is exothermic and yields a black powder within minutes. The reduction seems to be complete after 30–45 min, but reflux times of 2–3 h are normally used. The black materials are exceedingly reactive and will react quantitatively with bromobenzene at −78 °C in 5 min. In fact, chlorobenzene will react slowly at room temperature. The Grignard reactions are carried out by injecting the aryl halide or alkyl halide directly into the flask used to prepare the black materials. Relatively small changes in reactivities were noted if the solvent was changed to DME (dimethoxyethane) or diglyme or if $MgBr_2$ or MgI_2 were reduced instead of $MgCl_2$.

In attempting to understand the effects of the alkali salt generated in the reduction on the reactivity of the metal powder, we added additional alkali metal salts either before or after the reduction of $MgCl_2$. When KI was added prior to the reduction of $MgCl_2$, a suspension of more reactive black material was obtained. This "KI-activated magnesium" powder readily reacted with *p*-chlorotoluene at room temperature. Several different salts were tried to see if they had a similar activating effect. However, only in the cases of KI and NaI was any effect noted.

The exact origin of this activation is still under investigation, though it is clear that reduction in the presence of KI yields magnesium of much smaller particle size. ESCA clearly shows the magnesium to be in the zerovalent state, and particle size analysis indicated the average size was 15 mμ. SEM photographs give the appearance of an almost spongelike material (see Figure 1).

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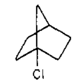
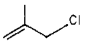
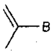
Table I
Reactions of Activated Magnesium with Various Halides[a]

Halide	Mg/halide	Mg/KI	Reaction temp, °C	Reaction time, min	% yield Grignard[b] Mono	% yield Grignard[b] Di	% yield[c] -CO_2H
1,4-$Br_2C_6H_4$	4	2	25	15		100	
1-Cl,4-Br-C_6H_4	4	2	25	15	100	10	
				60	100	57	
				120	100	100	
1,4-$Cl_2C_6H_4$	4	2	25	15	100	15	
				120	100	30	
1,4-$Cl_2C_6H_4$	2	2	25	5	70	0	
				60	86	0	
				180	90	0	89[d]
$C_8H_{17}Br$	2		25	5	100		81[e]
t-BuCl	2		25	10	100		52[e]
				60			
	1.7	2	66	15	11		
				90	42		
				360	74		63[d]
	2		25	60			82[e]
	2		25	5	100		71[e]
1-F,4-MeC_6H_4	4	2	66	60			69
$C_8H_{17}F$	2	2	25	180			89

[a] Mg source was either $MgCl_2$ + K or $MgCl_2$ + KI + K, THF solvent, refluxed 2–3 h prior to halide addition. [b] Yield by vpc after hydrolysis. [c] Yield of isolated carboxylic acid. [d] Yield based on Grignard. [e] Yield based on starting halide.

We have examined reactions of the "activated magnesium" and the "KI-activated magnesium" with various alkyl and aryl halides.[4] The results of these studies are summarized in Table I. The table clearly demonstrates the high reactivity of the magnesium and "KI-activated" magnesium produced by this reduction process. Perhaps the most striking reaction is that with *p*-fluorotoluene. Until this report, all efforts to prepare the Grignard reagent of fluorobenzene had failed. The Grignard reagents generated from the highly reactive magnesium appear to react normally with various substrates. Reaction with H_2O gives the hydrocarbon, addition of CO_2 gives the carboxylic acid, and addition of carbonyl-containing molecules gives the expected addition products. The high reactivity of the magnesium allows Grignard reactions to be carried out at −78 °C or lower and allows the Grignard reaction to be extended to heat-sensitive compounds. Other reactions that have been reported for the highly reactive magnesium include reaction with butadiene[37b] and reaction with ketones to yield pinacols.

Kalbunde has recently shown that cocondensation of Mg or Ni with solvents such as THF or hexane yield, upon warming, active metal slurries.[38] The Mg–THF slurries produced in this manner appear to be quite reactive and should prove to be of general value in the generation of Grignard reagents. Although the reactivity of this Mg is high, it is not nearly as reactive as the Mg produced by the potassium reduction of $MgCl_2$.

Activated Zinc

We have found that essentially the same procedure used to generate the activated magnesium can be used to generate "activated zinc". The most active zinc can be generated from anhydrous $ZnCl_2$, potassium, and THF.[2,11] The reduction is very exothermic, and extreme care must be exercised during the initial stages. It is best not to stir the mixture during the first part of the reduction. The mixture should be heated very slowly at first, and the heat should be removed just as the potassium melts. After the initial vigorous reaction is over, the reaction is heated at reflux with stirring for 2 h. A deep black zinc powder is generated during the reduction. Particle size analysis indicates the average size is 17 mμ, and powder patterns show both the characteristic lines of KCl and ordinary zinc metal.

The direct reaction of zinc metal with organic iodides dates back to the work of Frankland.[39] Several modifications have been suggested since that time to increase the reactivity of the metal. The majority of these modifications have employed zinc–copper couples[40–44] or sodium–zinc alloys.[45] Some recent work has indicated that certain zinc–copper couples will react with alkyl bromides to give modest yields of dialkylzinc compounds.[46,47] However, all attempts to react zinc with aryl iodides or bromides have met with failure. We have found that "activated zinc" will react rapidly with alkyl bromides in refluxing THF and, after distillation, will give quantitative yields of the corresponding dialkylzinc compounds. Also, it was found that "activated zinc" will react rapidly with iodobenzene and even with bromobenzene.[2]

Recent work has shown that activated zinc reacts very rapidly with α-bromoacetates at room temperature or lower, and the resulting organozinc compounds react with carbonyl compounds (Reformatsky reaction) in

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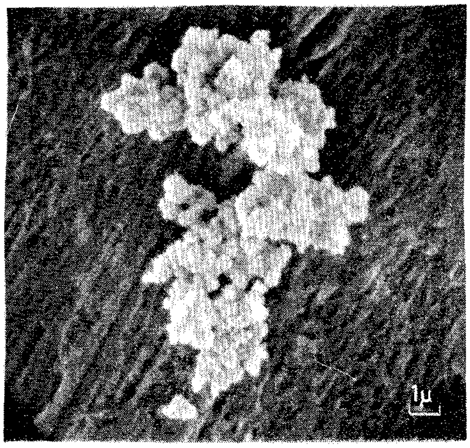
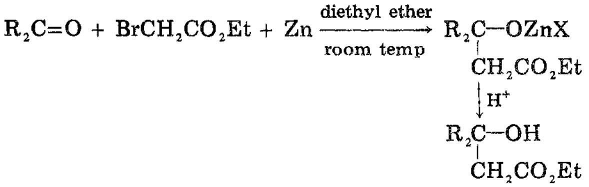


Figure 2. Activated indium prepared by reduction of $InCl_3$ with potassium in xylene.

high yields.[11] It was found that the reaction proceeded much better in diethyl ether than in THF. If THF is



$$\begin{array}{l} R_2C{=}O + BrCH_2CO_2Et + Zn \xrightarrow[\text{room temp}]{\text{diethyl ether}} R_2C{-}OZnX \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad | \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad CH_2CO_2Et \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad \downarrow H^+ \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad R_2C{-}OH \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad | \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad CH_2CO_2Et \end{array}$$

used to carry out the reaction, yields on the order of 65% result. The best results are obtained by first generating the activated zinc in THF using the standard procedure. The THF is stripped off and dry diethyl ether is added. A 1:1 mixture of ketone or aldehyde and α-bromo ester is then added dropwise at ice-bath temperatures. Finally, the reaction mixture is stirred at room temperature for 1 h, followed by normal workup procedures. This procedure gives uniformly high yields, mostly above 95%, whereas the conventional method gives yields that are generally much lower, often in the range of 50–60%. It is noteworthy that both aldehydes and ketones give high isolated yields of the resulting α-hydroxy ester.

Activated Indium

The use of indium metal in organic or organometallic synthesis is at best limited. Recently Gynane, Waterworth, and Worrall[48] reported the successful reaction of methyl, ethyl, and propyl bromides and iodides with metallic indium. The reaction, however, was very slow, requiring 1–3 days for the iodides and 3–5 days for the bromides, and produced a product mixture of R_2InX and $RInX_2$.

We have found that the reduction of anhydrous $InCl_3$ with potassium in refluxing xylene produces finely

$$InCl_3 + 3M \rightarrow In^* + 3MCl$$
$$M = K, Na$$

divided black indium metal of exceptional reactivity.[6,7,9] In this case, ethereal solvents do not work, as there appears to be extensive reductive cleavage of the solvent. The reduction requires from 4 to 6 h and is carried out under an argon atmosphere. Particle size determinations on this material indicated a range of 10 μ to 0.2 μ, with the average particle size being 4.0 μ. The activated indium shows a normal powder pattern of both indium metal and also the KCl. A scanning electronmicroscope photograph of the activated indium can be seen in Figure 2. Once again, the activated metal particles appear to be conglomerates of small crystals and to have very high surface areas.

Reaction of the activated indium with alkyl iodides

$$In^* + RI \xrightarrow[2\ h]{80\ ^\circ C} R_2InI + InI \quad \text{97–100\% yield}$$
$$R = Me, Et$$

was found to proceed very rapidly, producing an almost quantitative yield of a single product, the dialkylindium iodide.[6] Furthermore, it was found that the activated indium would react with neat iodobenzene to produce high yields of diphenylindium iodide.[9] In fact, the activated indium will react slowly with bromobenzene. Additional studies showed that the activated indium reacted readily with α-halo esters to give the organoindium product.[10] This new reagent was found to add to the carbonyl group of ketones and aldehydes to give α-hydroxy esters in high yields.

$$2In + 2BrCH_2CO_2Et \xrightarrow[55\ ^\circ C]{\text{xylene}} BrIn(CH_2CO_2Et)_2 + InBr$$

Additional evidence of the high reactivity of the indium powder can be seen in its reaction with organomercury compounds.[9] For example, Dennis[49] pre-

$$2In^* + 3R_2Hg \rightarrow 2R_3In + 3Hg$$
$$R = \text{alkyl, aryl}$$

pared $(CH_3)_3In$ from indium metal and $(CH_3)_2Hg$ by heating at 100 °C for 8 days, and no yield was reported. However, when $(CH_3)_2Hg$ was allowed to react with the activated indium metal, the reaction reached 76% yields after only 3 h at 100 °C. Similarly, the preparation of the triarylindium compounds is greatly facilitated by using the activated indium metal, and the yields are essentially quantitative.

Activated Thallium

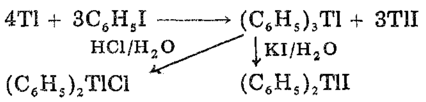
We have found that reduction of TlCl in xylene with potassium yields a finely divided black thallium powder

$$TlCl + K \xrightarrow[24\ h]{\text{refluxing xylene}} Tl + KCl$$

of exceptional reactivity.[27] The choice of solvent and thallium salt seem to be particularly important. Reaction of this thallium powder with iodobenzene when the ratio of iodobenzene to thallium is 1.5 leads to high yields of biphenyl. An interesting effect is noted if the

$$2Tl + 2C_6H_5I \xrightarrow[140\ ^\circ C,\ 24\ h]{\text{xylene}} C_6H_5\text{-}C_6H_5$$

reaction is run with an excess of thallium. In this case, with a ratio of iodobenzene to thallium of 0.3, the main product is triphenylthallium, as indicated by the final hydrolysis product.



$$\begin{tikzcd}[column sep=small] 4Tl + 3C_6H_5I \arrow[r] & (C_6H_5)_3Tl + 3TlI \arrow[dl, "HCl/H_2O"'] \arrow[d, "KI/H_2O"] \\ (C_6H_5)_2TlCl & (C_6H_5)_2TlI \end{tikzcd}$$

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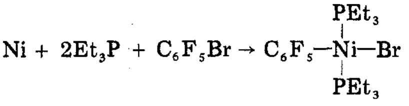
Activated Nickel, Palladium, and Platinum

As was pointed out in the introduction, the properties of the metals produced by this reduction method are highly dependent on the various parameters of the reaction, i.e., solvent, anion, reducing agent, etc. This turned out to be particularly true in the case of the transition metals Pt, Ni, and Pd.[26]

Initially we tried the standard approach of reduction of NiI_2, $NiBr_2$, or $NiCl_2$ with potassium in refluxing THF. Finely divided black nickel powders were obtained; however, they showed rather limited reactivity toward oxidative addition to carbon–halogen bonds. Similar results were found with palladium and platinum.

However, in the presence of a triaryl- or trialkylphosphine, the reduction yields a highly reactive metal slurry. When triethylphosphine is added to NiI_2 in THF, the highly soluble diiodobis(triethylphosphine)nickel(II) complex is formed. Addition of 2 mol of potassium to this mixture followed by refluxing yields a very fine black metal slurry of nickel. The reduction time is very dependent upon the type of phosphine used. For example, when triethylphosphine or triphenylphosphine were used the reduction times were approximately 20 and 2 h, respectively.

Not only is the particle size smaller when the reduction is carried out in the presence of the triethylphosphine but the reactivity of the metal toward oxidative additions is greatly enhanced. Upon the addition of pentafluorobromobenzene to the black nickel slurry a rapid reaction occurred, yielding bromopentafluorophenylbis(triethylphosphine)nickel(II) in 60% yield.



$$\mathrm{Ni} + 2\mathrm{Et_3P} + \mathrm{C_6F_5Br} \rightarrow \mathrm{C_6F_5}{-}\underset{\mathrm{PEt_3}}{\overset{\mathrm{PEt_3}}{\mathrm{Ni}}}{-}\mathrm{Br}$$

Nickel slurries produced by reducing NiI_2 in the presence of triphenylphosphine reacted with pentafluorobromobenzene at −78 °C to yield 46% of the bromopentafluorophenylbis(triphenylphosphine)nickel(II).

One additional reaction which further demonstrates the high reactivity of the nickel powders is with triethyl phosphite. Triethyl phosphite was added to the nickel powder at −78 °C. After 10 min, the mixture was warmed to room temperature and stirred for 1 h. Workup of the reaction mixture yielded over 40% of the tetrakis(triethyl phosphite)nickel(0) complex.

The reduction of $PdCl_2$ with potassium in the presence of triethylphosphine in THF yields a highly reactive black palladium slurry. Addition of pentafluorobromobenzene to the metal slurry yielded 76% of the bromopentafluorophenylbis(triethylphosphine)palladium(II). The reaction has been extended to unreactive halides. For example, the palladium slurry reacted with chlorobenzene to give the chlorophenylbis(triethylphosphine)palladium(II) in 54% yield. In a similar manner, highly reactive platinum slurries can be prepared by reduction of platinum halides in the presence of phosphines. The addition of pentafluorobromobenzene to the platinum slurry yielded *trans*-bromopentafluorophenylbis(triethylphosphine)platinum(II) in 40% yield. The reaction has been extended to other aryl halides.

Activated Chromium

The formation of metal carbonyls by the direct reaction of the metal with CO at elevated temperatures and pressures is a well-established procedure for a wide variety of metals. However, for certain metals this procedure fails due to the low reactivity of the metal. Chromium is such a metal, and all attempts to react the metal with CO have failed to yield any $Cr(CO)_6$. It was recently shown that highly reactive chromium metal powders can be generated by the reduction process.[8] As with In and Al, reductions of chromium salts in THF failed due to the high reactivity of Cr(II) salts with organic ethers. However, reduction of $CrCl_3{\cdot}3THF$ in benzene yielded highly reactive black chromium powders. The reactivity of the chromium powder was found to be increased by carrying out the reduction in the presence of KI. The benzene was stripped off after the reduction was complete, and then THF was added to the black powder. The resulting slurry was added to an autoclave and reaction with CO gave yields of $Cr(CO)_6$ of 50% or better.

Other Metals

In addition to the above metals, we have prepared several other highly reactive metals via the reduction procedure. Aluminum powder generated from the reduction of $AlCl_3$ in xylene reacts rapidly with aryl halides. For example, bromobenzene reacted quantitatively in 5 min in xylene at 140 °C to give the corresponding phenylaluminum halides.[5] It also has been found that aluminum powders react with ketones and aldehydes to give high yields of pinacols.[50] Other metals that we have generated by the reduction process and that appear to have high reactivity include Cd, Sn, Pb, Fe, and Co. We have found that $TiCl_4$ upon reduction gave highly reactive black powders which readily undergo oxidative addition to aryl–halogen bonds.[50] McMurry has recently reported that Ti powders generated by our procedure could be used to reductively couple aldehydes or ketones to the corresponding olefins in high yields.[51] Also, treatment of 1,2-diols with the highly reactive Ti powders gave the corresponding olefins in high yields.[51]

Summary

The reduction of metal salts in ethereal or hydrocarbon solvents is a relatively simple procedure which requires very inexpensive equipment. The high reactivity of the metals generated by this procedure has extended existing reactions to many new classes of compounds. In some cases, the highly reactive metal powders have opened new areas of chemistry. We expect that the basic procedure will be applicable to many other metals not yet examined. As already pointed out and demonstrated for Mg, Ni, Pd, and other metals, it is likely that this approach will lead to many different types or degrees of reactivity for each metal. We have already shown that for many metals the reactivity of the metal powder is highly dependent on the particular reaction conditions. To date, this approach has been somewhat of a trial and error approach. We fully expect, however, that as the areas of surface science and colloidal chemistry develop, the

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(50) R. D. Rieke and L. Chao, to be published.

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reaction conditions can be adjusted to tailor-make the particular particle size and chemical reactivity desired. Thus, we expect this area of research to be a continuing and fruitful one.

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Trifyl Activation in Organic Synthesis

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The sulfonyl group is especially valuable in synthetic organic chemistry because of its unusually versatile reactivity. It functions as both an electrophile and as a nucleophile-leaving group. At the same time, the electron-withdrawing power of the sulfonyl group stabilizes adjacent negative charge and activates olefins for nucleophilic addition or cycloaddition. All of these properties (except nucleophilicity) are enhanced as the electronegativity of the sulfonyl substituent is increased. It is this factor that directed our interest to the trifluoromethanesulfonyl group (CF_3SO_2–); hereafter referred to as *trifyl* and symbolized as Tf), which is reported to be one of the strongest neutral electron-withdrawing groups known.[1,2]

The large inductive effect of the trifluoromethyl group is illustrated by comparison of pK_a values (Table I[2-7]) with those of the common benzenesulfonyl derivatives. In general, this strongly enhanced electron withdrawal causes remarkable facilitations of known sulfonyl reactivity and leads to some previously unknown reactions. Furthermore, the trifyl group has the synthetic value of being inert to a wide variety of reaction conditions.

The primary electrophilic trifyl reagent is the very reactive triflic anhydride (($(CF_3SO_2)_2O$), obtained from P_2O_5 dehydration of triflic acid (CF_3SO_2OH). The primary nucleophilic form is triflinate anion ($CF_3SO_2^-$), obtained from iodide reduction of CF_3SO_2Cl.[8,9] Both reagents are easily prepared and stable.[10] In general the reactions cited for these reagents involve initial attachment of the trifyl group to a molecule followed by construction or refunctionalization reactions and finally removal of the trifyl group when no longer needed.

From the outset it was apparent that trifyl activation would involve either or both of the atoms α and β to the trifyl group, i.e., Y and/or Z in the molecular generalization $Y–Z–SO_2CF_3$. The reactions include making or breaking the Y–Z and $Z–SO_2CF_3$ single bonds as well as addition or elimination to Y=Z double bonds. The consequent variety of molecular types is illustrated in Table II for the common atoms, and this format is used here to present our initial findings. The dashes in the table imply potentially useful compounds as yet unexplored; some are under current study in our laboratories.

Table I
Comparison of pK_a Values: RSO_2Z

R	Z: CH_3[a]	NH_2[a]	OH	H[c]
Ph	29.0[2]	16.7[3]	0.70[4,c]	2.76[6]
CF_3	18.8[2]	9.75[3]	<–11[5,b] (0.31[3,a])	~0[7]

[a] Me_2SO. [b] HOAc. [c] H_2O.

Table II
Permutations of Y-Z-Tf

	Z \ Y	C	N	O	P	S
Triflones	C	*a*	–	–	–	*a*
Triflamides	N	*a*	*a*	*a*	–	–
Triflates	O	*a*	*a*	*a*	*a*	*a*
	P	–	–	–	–	–
	S	–	–	–	–	–

[a] Examples studied to date.

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(10) Particular laboratory details for these and other related trifyl reagents and general details about their use in practice will be found in J. B. Hendrickson, K. W. Bair, P. L. Skipper, D. D. Sternbach, and J. Wareing, *Org. Prep. Proced. Int.*, in press.