Synthesis and Utilization of Organocopper(I) Ate Complexes from Grignard Reagents

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Organocopper(I) ate complexes can be prepared in high yield from methylcopper(I) and aliphatic or aryl Grignard reagents. The resulting complexes efficiently transfer the Grignard reagent derived primary, secondary, tertiary, or aryl group in reactions in acyl chlorides leading to ketones. This synthetic method is illustrated with procedures for $CH_3(CH_2)_{15}COCH_3$, $C_6H_5COC_6H_5$, $CH_3(CH_2)_2CH(CH_3)COCH_3$, $(CH_3)_3CCOC_6H_5$, p-$CH_3C_6H_4COC_6H_5$, $C_6H_5COCH_3$, $(CH_3)_3CCOC(CH_3)_3$, and $C_6H_5CO(CH_2)_3CH_3$. This reaction provides a general and useful alternative to syntheses of organocopper(I) ate complexes from organolithium reagents. Methylcopper(I) is shown to be significantly better than other copper(I) species for forming reactive organocopper(I) ate complexes from Grignard reagents.

Applications of organocopper(I) reagents in organic synthesis have expanded in recent years to include numerous alkylation reactions such as alkylation of alkyl halides, acyl halides, and α-halogenated carbonyl compounds.[1] These reactions and the well-established 1,4-conjugate addition of organocopper reagents to α,β-unsaturated carbonyls[2] make organocopper reagents versatile synthetic intermediates.[3] However, the principal synthetic route to reactive organocopper(I) ate complexes is still the reaction of an alkyllithium reagent with a free or complexed copper(I) salt. In general, the more readily available Grignard reagents cannot be used in place of an alkyllithium reagent in these syntheses.[1,4] Other routes to reactive organocopper(I) compounds from organomercurials[5] and organoboranes[6] have recently been reported, but these methods are not as generally applicable as the reaction of organolithium reagents with copper(I) salts.

We wish to report a useful alternative to the above syntheses that employs the reaction of a Grignard reagent with preformed methylcopper(I) to generate an organocopper(I) ate complex capable of selectively transferring the Grignard reagent derived alkyl group in synthetically useful reactions. The utility of these Grignard reagent derived organocopper(I) reagents in the synthesis of ketones from acid chlorides is described.[7] We have also comparatively evaluated routes leading to reactive organocopper(I) reagents from copper(I) species other than methylcopper(I).

Results

Methylcopper(I), prepared from a THF suspension of cuprous iodide and methyllithium, reacts in high yield (vide infra) with Grignard reagents to give organocopper(I) ate complexes. These complexes can be formed equally well from primary, secondary, tertiary, and aryl Grignard reagents. The organocopper(I) ate complexes so formed have been demonstrated to have useful reactivity toward acyl halides, alkyl halides,[8] and α,β-unsaturated ketones.[9] Representative examples of the reaction of these ate complexes with acyl chlorides leading to ketones are detailed in Table I.

In a typical procedure, 50 mmol of preformed methylcopper(I) in 150 ml of THF was allowed to react with 50 mmol of *tert*-butylmagnesium bromide at −78 °C to yield, after warming to 25 °C, a suspension of an organocopper(I) ate complex. Addition of 50 mmol of benzoyl chloride by syringe to this purple suspension of *tert*-butyl(methyl)copper(I) magnesium bromide[10] at −78 °C gave a yellow suspension. After warming to room temperature and stirring for 1 h, workup (see Experimental Section) and simple distillation yielded 97% of ketone product which was a mixture of acetophenone (10%) and pivaloylphenone (90%).

As can be seen from the data in Table I, it is possible to achieve significant selectivity in the transfer of the alkyl group originally bound to magnesium if the aklylation reaction is carried out at −78 °C with stoichiometric amounts of acyl chloride and copper reagent. However, since the by-product resulting from transfer of a methyl group can often be easily separated from the desired product, excess acyl chloride can be used in many cases to ensure complete reaction. Steric factors in the acyl chloride or organocopper(I) ate complex also appear to be unimportant in this reaction as demonstrated by the comparable yields of acetophenone, 2,2-dimethyl-1-phenyl-1-propanone, and 2,2,4,4-tetramethyl-3-pentanone.

These Grignard reagent derived organocopper(I) ate complexes are qualitatively different from their lithium diorganocuprate analogues in several respects. First, although the magnesium containing ate complexes are soluble as dilute (ca. 0.2 M) solutions at 25 °C, they form suspensions at −78 °C in contrast to lithium dialkylcuprates. Second, the thermal stability of magnesium containing ate complexes is somewhat greater than that of corresponding lithium diorganocuprates. For example, lithium di-*tert*-butylcopper(I) decomposes on warming to 25 °C[11] while *tert*-butyl(methyl)copper(I) magnesium bromide is stable for at least 30 min at 25 °C. Although the reason for this slightly greater thermal stability is unknown, it is worthwhile to note that incorporation of a methyl group into lithium dialkylcuprates enhances the thermal stability of the resulting lithium dialkylcuprate.[12] The observation that ternary copper(I) ate complexes containing mercury(II) have enhanced thermal stability suggests that the magnesium may also be important in increasing the thermal stability of these ate complexes.

The selectivity in the transfer of the alkyl groups observed in these reactions parallels that observed in alkylation reactions of these ate complexes with alkyl halides.[8] Comparable selectivity has been observed with lithium methyl(vinyl)copper(I) in 1,4-conjugate addition reactions suggesting that this preference for transfer of alkyl groups other than methyl may be general.[13,14]

It is evident from the isolated and GLC measured yields that this procedure is comparable to the synthesis of ketones from acid chlorides and lithium diorganocuprates. Since Grignard reagents are more readily available than alkyllithium reagents, this synthesis represents a reasonable alternative route to ketones from carboxylic acid chlorides. The procedure is also compatible with a variety of functional groups, as demonstrated by the stability of methyl benzoate and acetophenone to n-butyl(methyl)copper(I) magnesium bromide under the reaction conditions (see Experimental Section). A further advantage of these procedures is that high yields can be obtained without the necessity for excess reagents. A limitation of this procedure is that the formation of the by-

Table I. Ketones Synthesized from Grignard Reagents Using Organocopper(I) Ate Complexes "$R(CH_3)CuMgX$" and Acyl Chlorides

Grignard reagent (R)	Registry no.	Acyl halide	Registry no.	Product	Registry no.	Isolated yield, %[a]
$CH_3(CH_2)_{14}CH_2MgBr$	112-82-3	CH_3COCl	75-36-5	$CH_3(CH_2)_{15}COCH_3$	7373-13-9	75
$CH_3CH_2CH_2CH_2MgBr$	109-65-9	C_6H_5COCl	98-88-4	$CH_3(CH_2)_3COC_6H_5$	1009-14-9	85[b]
$CH_3(CH_2)_2CH(CH_3)MgBr$	107-81-3	CH_3COCl		$CH_3(CH_2)_2CH(CH_3)COCH_3$	2550-21-2	90
$(CH_3)_3CMgBr$	507-19-7	C_6H_5COCl		$(CH_3)_3CCOC_6H_5$	938-16-9	93[b]
p-$CH_3C_6H_4MgBr$	106-38-7	C_6H_5COCl		p-$CH_3C_6H_4COC_6H_5$	134-84-9	79
C_6H_5MgBr	108-86-1	$(CH_3)_3CCOCl$	3282-30-2	$C_6H_5COC(CH_3)_3$		100[c]
$(CH_3)_3CMgBr$		$(CH_3)_3CCOCl$		$(CH_3)_3CCOC(CH_3)_3$	815-24-7	90[d]
C_6H_5MgBr		CH_3COCl		$C_6H_5COCH_3$	98-86-2	84
C_6H_5MgBr		C_6H_5COCl		$C_6H_5COC_6H_5$	119-61-9	96[c]

[a] These yields are based on Grignard reagent. The product ketones were identified by their physical (melting point, boiling point) and spectroscopic properties (ir, NMR). In all cases, gas chromatography showed the isolated products to be >98% pure. Isolated ketones were also characterized by formation of a 2,4-dinitrophenylhydrazone or semicarbazone derivative. [b] One equivalent of acyl chloride per equivalent of Grignard reagent was used to minimize formation of acetophenone. [c] Yield determined by gas chromatography. [d] The isolation of pure product in this example was hampered by co-distillation of pinacolone.

Table II. Utility of Copper(I) Compounds, RCu, in Forming Reactive Ate Complexes with n-Butylmagnesium Bromide

RCu	Registry no.	Yield of ketone product after reaction with benzoyl chloride, %[a]	Reactivity toward methyl benzoate at 25 °C (% methyl benzoate recovered)
$(CH_3)_3$-$CC{\equiv}CCu$	40575-23-3	28 (74)[b]	99
$(CH_3)_3COCu$	35342-67-7	0[c] (94)[b]	102
C_6H_5SCu	1192-40-1	0[c] (79)[b,d]	101
ICu	7681-65-4	46[e]	45[e]
CH_3Cu	1184-53-8	85[d]	100

[a] Yields determined by GLC under comparable conditions using octadecane as an internal standard. These yields are based on the assumption that only one alkyl group can be transferred per copper atom. [b] This yield was obtained using n-butyllithium instead of n-butylmagnesium bromide. [c] No 1-phenyl-1-pentanone was detected by GLC. [d] This is an isolated yield. [e] The presence of a dark suspension suggested that decomposition of the organocopper(I) had occurred under the reaction conditions.

product methyl ketone cannot be completely suppressed and the separation of small amounts of methyl ketone from the product of interest may be difficult in some cases.

Because of the conflicting reports in the literature concerning the efficacy of Grignard reagents for the synthesis of reactive organocopper(I) compounds, we briefly examined the use of starting copper(I) species other than methylcopper(I). The results of these studies are listed in Table II. As can be seen from the stability of methyl benzoate under comparable conditions, an equilibrium concentration of Grignard reagent is not present in any of these cases. This implies complex formation. Nonetheless, reaction of these complexes with benzoyl chloride under comparable conditions to those discussed above leads to significantly lower yields of ketone product. The lower reactivity for n-butyl-(3,3-dimethylbutynyl)-, n-butyl(*tert*-butoxy)-, and n-butyl(thiophenoxy)copper(I) magnesium bromide relative to n-butyl(methyl)copper(I) magnesium bromide is in accord with previous studies of the relative reactivities of mixed lithium cuprates.[14]

Conclusion

Reaction of methylcopper(I) with a wide variety of Grignard reagents leads to organocopper(I) ate complexes whose reactivity is comparable to that of lithium diorganocuprates. These Grignard reagent derived cuprates have been shown to be effective in alkylation of alkyl halides and in alkylation of acyl chlorides to yield ketones. These Grignard reagent derived cuprates show both useful selectivity and efficiency in their reactions, transferring the alkyl group originally bound to magnesium preferentially and in high yield without the need for excess reagent. In addition, the thermal stability of these "alkyl(methyl)copper(I) magnesium halide" reagents is somewhat greater than that of their lithium dialkylcopper(I) analogues. Methylcopper(I) is also shown to be the most useful copper(I) species for the formation of reactive organocopper(I) reagents from organomagnesium compounds.

Experimental Section

General Methods. All reactions of air and water sensitive organometallics were carried out in flame-dried glassware under prepurified nitrogen using standard techniques.[15] Tetrahydrofuran and other ethereal and hydrocarbon solvents were distilled from a purple solution or suspension of disodium benzophenone dianion prior to use. Melting points were determined on a Thomas-Hoover capillary melting point apparatus and are uncorrected. NMR spectra were recorded on a Varian T-60 spectrometer. Infrared spectra were taken on sodium chloride plates or in sodium chloride cells on a Beckman IR-8 spectrometer. A Perkin-Elmer Model 3920 gas chromatograph was used for GLC analyses. A 0.32 by 183 cm 3% SP-2300 on 100/120 Supelcoport column was used for both qualitative and quantitative analyses. Lithium reagents were purchased from Alfa Inorganics Inc. Lithium reagents and Grignard reagents were analyzed by the method of Watson and Eastham.[16] When the difference between total base as determined by titration with standard 0.1 M HCL and active organometallic exceeded 10% of the active organometallic, the solutions were discarded. 1-Bromohexadecane was purchased from Air Products and Chemicals. Other organic chemicals were purchased from the Aldrich Chemical Co. Acid chlorides were redistilled prior to use. Magnesium turnings for the preparation of Grignard reagents were purchased from Fisher Scientific. Cuprous iodide was generally purified prior to use[17] although freshly opened bottles were also found to be satisfactory.

3,3-Dimethylbutyne was prepared in 90% yield according to the procedure of Collier and Macomber.[18]

General Procedure for the Synthesis of Ketones as Illustrated by the Synthesis of 4-Methylbenzophenone. 4-Methylphenylmagnesium bromide was prepared from magnesium turnings and 4-methylbromobenzene in ether using standard procedures. A bright yellow suspension of methylcopper(I) was prepared in a 1-l., flame-dried, three-necked, round-bottomed flask equipped with an overhead stirrer and low-temperature thermometer by the reaction of 30 ml of a 1.73 N (51.9 mequiv) ether solution of methyllithium (0.11 N in residual base) with a −78 °C suspension of 9.6 g (50.8 mmol) of cuprous iodide in 100 ml of THF. The bright yellow color characteristic of methylcopper(I) formed when this reaction mixture was warmed to 25 °C. After this yellow suspension was cooled to −70 °C with a dry ice–acetone bath, 26 ml of a 1.96 N (51.0 mequiv) ether solution of 4-methylphenylmagnesium bromide was added with a syringe. The resulting suspension was allowed to warm to 25 °C with stirring after removal of the dry ice–acetone bath. The resulting deep purple solution was cooled to −78 °C and 13 ml (112 mmol) of benzoyl chloride in 30 ml of THF was added dropwise by syringe. The reaction mixture was then warmed to 25 °C with stirring and allowed to stir for an additional 0.5 h. Addition of 8 ml of absolute methanol quenched any unreacted organometallic and benzoyl chloride. The reaction mixture was then added to 600 ml of saturated aqueous ammonium chloride solution. Stirring this mixture for 2 h dissolved any copper salts and facilitated the subsequent extractions.[19] The ethereal phase was then separated and the aqueous portion was washed with two 100-ml portions of ether. The combined organic fractions were washed once with 100 ml of 0.1 N aqueous sodium thiosulfate, three times with 100 ml of 1.0 N sodium hydroxide, and once with 200 ml of saturated sodium chloride, and then dried (K_2CO_3). The product 4-methylbenzophenone was isolated (7.8 g, 79% yield) by distillation using a short-path distillation apparatus and had bp 120–130 °C (0.6 Torr) [lit.[20] bp 311–312 °C (720 Torr)]; ir (CH_2Cl_2) 1670 cm^{-1}; NMR ($CDCl_3$) δ 7.1–7.9 (m, 9 H), 2.4 (s, 3 H). The 2,4-dinitrophenylhydrazone of this product had mp 198–199 °C (lit.[20] mp 199–200 °C).

1-Phenyl-1-pentanone was prepared from *n*-butylmagnesium bromide according to the procedures described above with the slight modification that only 1 equiv of benzoyl chloride per equivalent of starting Grignard reagent was used to minimize acetophenone formation. The product 1-phenyl-1-pentanone was purified by fractional distillation through a 50 by 1 cm Holtzman column packed with a spiral wire and was isolated in 85% yield: bp 146–150 °C (38 Torr) [lit.[20] bp 135–140 °C (25 Torr)]; ir (neat) 1690 cm^{-1}; NMR (CCl_4) δ 7.1–8.0 (m, 5 H), 2.56 (t, 2 H), 1.0–2.0 (m, 4 H), 0.97 (t, 3 H). A 2,4-dinitrophenylhydrazone derivative prepared from the purified product had mp 163–164 °C dec after several recrystallizations from 95% ethanol (lit.[20] mp 166 °C). Gas chromatography showed that the distilled product contained less than 5% acetophenone as the only impurity.

3-Methyl-2-hexanone, prepared from 2-pentylmagnesium bromide according to the procedure described above, was isolated in 90% yield (5.1 g) after distillation and had bp 142–146 °C (lit.[20] bp 142–145 °C); ir (neat) 1710 cm^{-1}; NMR ($CDCl_3$) δ 2.47 (m, 1 H), 2.05 (s, 3 H), 0.9–1.8 (m, 4 H), 1.03 (d, 3 H), 0.93 (t, 3 H).

2-Octadecanone. Following the general procedures described above, hexadecylmagnesium bromide and methylcopper(I) were allowed to react to give an ate complex which was then allowed to react with excess acetyl chloride to give 20 g (75%) of 2-octadecanone which was isolated as a pure product after recrystallization from ethanol. The product 2-octadecanone had mp 49–50 °C (lit.[20] mp 52 °C) and ir (CCl_4) 1711 cm^{-1}. The identity of the product was confirmed by preparation of a semicarbazone derivative having mp 124–125 °C (lit.[20] mp 125.5–126 °C).

2,2-Dimethyl-1-phenyl-1-propanone was prepared from *tert*-butylmagnesium bromide and benzoyl chloride as described above. Traces of acetophenone in the distilled ketone product were removed by column chromatography using silica gel. The product ketone had bp 216–220 °C (lit.[20] bp 219–221 °C); ir (neat) 1682 cm^{-1}; NMR (neat) δ 7.1–8.0 (m, 5 H), 1.27 (s, 9 H). The product was further characterized by the preparation of a 2.4-dinitrophenylhydrazone derivative having mp 192–193 °C dec (lit.[20] mp 194 °C).

This ketone was also prepared on a 1-mmol scale from phenylmagnesium bromide and pivaloyl chloride following similar procedures. Analysis by GLC using nonadecane as an internal standard showed that 2,2-dimethyl-1-phenyl-1-propanone had been formed in quantitative yield.

2,2,4,4-Tetramethyl-3-pentanone was prepared on a 1-mmol scale from *tert*-butylmagnesium bromide and pivaloyl chloride according to the procedure described above in 90% yield as determined by gas chromatography using *n*-decane as an internal standard.

Benzophenone was prepared from phenylmagnesium bromide and benzoyl chloride according to the procedures described above. Gas chromatographic analysis of a 1-mmol scale reaction using *n*-docosane as an internal standard showed that the product ketone had formed in 96% yield.

Acetophenone was prepared from phenylmagnesium bromide and acetyl chloride according to the procedure described above. The product acetophenone was isolated by distillation in 83% yield and had bp 200–204 °C (lit.[20] bp 202 °C); ir (neat) 1691 cm^{-1}; NMR ($CDCl_3$) δ 7.2–8.0 (m, 5 H), 2.50 (s, 3 H); 2,4-dinitrophenylhydrazone mp 241–242 dec (lit.[20] mp 237 °C).

Evaluation of Other Copper(I) Salts in the Synthesis of Reactive *n*-Butylcopper(I) Ate Complexes. Cuprous thiophenoxide, cuprous *tert*-butoxide, and 3,3-dimethylbutynylcopper(I) were prepared according to literature procedures.[7,14] One equivalent of 1.55 N *n*-butylmagnesium bromide in ether per equivalent copper(I) salt was added to a −78 °C suspension of the copper(I) species. Warming to room temperature then generated the butylcopper(I) ate complex of interest. The *n*-butyl(thiophenoxy)copper(I) magnesium bromide was a white suspension, the *n*-butyl(*tert*-butoxy)copper(I) magnesium bromide was a blue solution, the *n*-butyl(3,3-dimethylbutynyl)copper(I) magnesium bromide was a greenish solution, and the di-*n*-butylcopper magnesium bromide was a dark gray suspension. The reactivity of these resulting complexes was evaluated by addition of excess benzoyl chloride and subsequent GLC analysis for 1-phenyl-1-pentanone. Results of these experiments are detailed in Table II.

In similar experiments, the stability of methyl benzoate in the presence of these mixed ate complexes was evaluated by addition of a known amount of methyl benzoate and an internal GLC standard to the organometallic solution or suspension of interest. The stability of methyl benzoate to these various complexes is described in Table II and was determined by gas chromatography.

Stability of methyl benzoate and 1-phenyl-1-pentanone to *n*-butyl(methyl)copper(I) magnesium bromide was determined by the addition of known amounts of these compounds and appropriate internal standards to the ate complex formed by reaction of *n*-butylmagnesium bromide with methylcopper(I). These reaction mixtures were stirred for 1 h at −78 °C and 1 h at 25 °C. The organometallic species present was then quenched with methanol and the yield of recovered ketone or ester was determined by GLC. In several separate runs, both methyl benzoate and 1-phenyl-1-pentanone could be recovered in yields ranging from 94 to 100%.

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Registry No.—Methyl benzoate, 93-58-3; hexadecyl(methyl)copper(I) magnesium bromide, 59547-38-5; *n*-butyl(methyl)copper(I) magnesium bromide, 59532-66-0; 2-pentyl(methyl)copper(I) magnesium bromide, 59532-64-8; *tert*-butyl(methyl)copper(I) magnesium bromide, 59532-65-9; 4-methylphenyl(methyl)copper(I) magnesium bromide, 59532-62-6; phenyl(methyl)copper(I) magnesium bromide, 59532-63-7; *n*-butyl(thiophenoxy)copper(I) magnesium bromide, 59532-67-1; *n*-butyl(*tert*-butoxy)copper(I) magnesium bromide, 59532-60-4; *n*-butyl(3,3-dimethylbutynyl)copper(I) magnesium bromide, 59532-59-1; di-*n*-butylcopper magnesium bromide, 59532-61-5.

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(10) For convenience, we have named these ate complexes according to the stoichiometry involved in their formation. The actual structure and extent of aggregation of these complexes is not known.

(11) Significant amounts of decomposition were suggested by the variable amounts of ketone products formed upon reaction with benzoyl chloride (typical yields of pivaloylphenone ranged from 10 to 40%).

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Methylation of Thioanisoles and Anilines by 1-Methyl-2,5-diphenyl-1,4-dithiinium Tetrafluoroborate. Kinetics and Correlations[1]

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The kinetics of methyl transfer from 1-methyl-2,5-diphenyl-1,4-dithiinium tetrafluoroborate (**1**) to a series of thioanisoles (**2**) and to a comparable series of anilines (**5**) have been followed spectrophotometrically in acetonitrile under pseudo-first-order conditions at four temperatures for each compound. Derived second-order rate constants, Arrhenius equation constants, and activation thermodynamic parameters have been calculated for intra- and interseries comparison. Both series exhibited well-defined Hammett correlations ($\rho_S = -1.58 \pm 0.04$; corr coeff = 0.999 for the thioanisoles, and $\rho_N = -1.95 \pm 0.05$; corr coeff = 0.998 for the anilines) in which the ρ values were essentially constant over the range 25–80 °C. Specific rate constants for the thioanisole set ($k_S{}^X$) correlated well with those of the aniline set ($k_N{}^X$) via a linear equation: $\log k_S{}^X = m \log k_N{}^X +$ constant, where the slope m is approximated by the ratio of Hammett ρ values (ρ_S/ρ_N). Comparisons with literature data show that dimethyl sulfate is 2.3 times as reactive as **1** toward the thioanisoles, and that **1** is about 10 times as reactive as MeI toward the anilines.

Transmethylation reactions,[3,4] which play a normal role in the cobalamin-dependent biosynthesis of methionine[5] and in the transfer of intact methyl groups from *S*-adenosyl-L-methionine to various receptor substrates,[6] appear to be universally important in biological systems. In addition to the enzyme specificities involved, such reactions apparently depend upon a subtle interplay of relative nucleophilicities of nitrogen, sulfur, oxygen, and cobalt moieties which are not yet well understood. The very concept of nucleophilicity, considered as kinetic basicity, has defied precise quantification and various equations in the literature have been shown to be of limited value for predicting relative nucleophilic reactivity.[7] Some qualitative comparisons of the relative nucleophilicities of S, N, and Co in methyl transfers have been reported by Schrauzer[8] who used simple methylsulfonium, -ammonium, and -cobaloxime models. More recently, Coward and Sweet[9] provided the first detailed kinetic study of methyl transfer from substituted aryldimethylsulfonium perchlorates to various anionic and amine nucleophiles.

In our laboratory we have been particularly interested in the nucleophilicity of bivalent sulfur. Qualitatively, it is well known that simple dialkyl sulfides are easily methylated by methyl iodide, sulfate, or sulfonates to give the corresponding sulfonium salts.[10] Compounds such as thioanisole (**2**, X = H) or diphenyl sulfide, in which bivalent sulfur is bonded to one or two sp[2] carbons, are alkylated with more difficulty, requiring either methyl sulfate at elevated temperatures or methyl iodide in the presence of equimolar amounts of mercuric iodide,[11] silver tetrafluoroborate,[12] silver perchlorate, or silver 2,4,6-trinitrobenzenesulfonate.[13] These reagents all have limited scope for comparative kinetic studies, and indeed kinetic data in the literature are sparse. Second-order rate constants for the reactions of several dialkyl sulfides with methyl iodide have been reported by Pearson,[7] and a Hammett correlation for methylation of a series of substituted thioanisoles with dimethyl sulfate in benzyl alcohol at 45.2 °C has been published by Gosselck and Barth.[14]

We now wish to report a kinetic study of the methylation of variously substituted thioanisoles (**2**) and anilines (**5**) by 1-methyl-2,5-diphenyl-1,4-dithiinium tetrafluoroborate (**1**),[15] a parallel set of systems (eq 1 and 2, respectively) selected to measure the relative nucleophilicities of bivalent sulfur vis-à-vis trivalent nitrogen of a comparable reference series.