CLEAVAGE OF SOME ALKYL ARYL ETHERS BY TRIPHENYLSILYLLITHIUM

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Schorigin[1] was the first to report the cleavage of ethers by an organometallic compound. He found that ethylsodium reacted with diethyl ether at room temperature to give ethanol, ethylene and sodium ethoxide. Phenetole and anisole led to sodium phenoxide. At about the same time Grignard[2] reported that phenetole was cleaved by amylmagnesium bromide at 160° to give phenol. Organolithium reagents later were found to attack the simpler alkyl ethers, but much more slowly than organosodium compounds[3,*]. In general, olefin formation predominated over coupling with the organometallic reagent[4].

Silylmetallic reagents cleave epoxides[5] and cyclic alkyl ethers[6,7] with formation of the corresponding silicon-substituted carbinols. The methyl ether, 1,2-dimethoxyethane was cleaved by triphenylsilyllithium (I) to give methyltriphenylsilane[7]. Diphenyl ether is one of the few ethers which is not cleaved by (I), but is dimetalated to give *o,o'*-dicarboxydiphenyl ether in low yield subsequent to carbonation[7].

While attempting to metalate anisole with triphenylsilyllithium (I), alkylation of the silylmetallic compound was observed. The products isolated after the reaction

$$C_6H_5OCH_3 + \underset{(I)}{(C_6H_5)_3SiLi} \longrightarrow \underset{(II)}{(C_6H_5)_3SiCH_3} + C_6H_5OH$$

mixture had been warmed at 50° for 24 h were methyltriphenylsilane (II) and phenol. This interesting reaction suggested an extension to the next higher homologs, phenetole and phenyl *n*-propyl ether. However, even after extended reaction periods at higher temperatures, only a trace of cleavage was observed with the former ether and none with the latter.

The great difference in reactivity may involve several factors. The cleavage probably occurs through an S_N2 displacement mechanism with phenoxide ion being the leaving group. Such a reaction is sensitive to steric factors both around the carbon

$$(C_6H_5)_3Si^{\ominus} + R\overset{\frown}{-}O-C_6H_5 \longrightarrow (C_6H_5)_3SiR + C_6H_5O^{\ominus}$$

being attacked and of the anion, *i.e.*, the rate of displacement is decreased significantly by small increases in steric hindrance[8]. Triphenylsilyllithium (I) represents a very

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[*] For a general review concerning the cleavage of ethers, see ref. 4.

bulky grouping. In addition, it is probably highly solvated with tetrahydrofuran molecules increasing its bulk still more. The large size of (I) would amplify the increased steric hindrance arising from the change of methyl to ethyl or *n*-propyl, and the cleavage reaction was greatly retarded.

The cleavage reaction was carried out successfully with a number of aryl methyl ethers, and the results are summarized in Table 1. In every instance, methyltriphenylsilane (II) and the corresponding phenol were formed.

TABLE 1

REACTION OF TRIPHENYLSILYLLITHIUM WITH SOME ALKYL ARYL ETHERS

Ether	R_3SiLi	*Ratio of* R_3SiLi *to ether*	*Conditions*		*Yield Alkyl-* $SiPh_3$	*Yield (%) phenol*
			Temp. °C	*hours*		
Anisole	Triphenylsilyllithium	1:1	50	24	64.2	31.5[a]
Phenetole	Triphenylsilyllithium	1:1	50 + 60	24 + 72	0	Trace
Phenyl *n*-propyl ether	Triphenylsilyllithium	1:1	50	72	0	
p-Dimethoxybenzene	Triphenylsilyllithium	1:1	50	12	60.5	30.2
p-Dimethoxybenzene	Triphenylsilyllithium	2:1	50	24	57.8	37.0 mono[b] 15.2 di[c]
1-Methoxynaphthalene	Triphenylsilyllithium	1:1	50	10	48.5	58.2
2-Methoxynaphthalene	Triphenylsilyllithium	1:1	50	16	52.5	58.8
p-Chloroanisole	Triphenylsilyllithium	1:1	50	2	0[d]	Trace
p-Fluoroanisole	Triphenylsilyllithium	1:1	50	24	49.2[e]	30.5
2-Methoxynaphthalene	Dimethylphenylsilyllithium	1:1	50	24	35.9	34.4
Phenetole	Dimethylphenylsilyllithium	1:1	50	72	0	3.57[a]
Thioanisole	Triphenylsilyllithium	1:1	50	24	8.33[f]	0

[a] Identified as 2,4,6-tribromophenol.

[b] Hydroquinone monomethyl ether.

[c] Hydroquinone.

[d] The primary products of the reaction were hexaphenyldisilane (40.7 %) and *p*-anisyltriphenylsilane (5.73 %).

[e] There was also obtained *p*-anisyltriphenylsilane (1.09 %). No hexaphenyldisilane was isolated.

[f] Tetraphenylsilane (13.7 %) and hexaphenyldisilane (6.17 %) were also isolated.

Triphenylsilyllithium (I) cleaved one methyl group from *p*-dimethoxybenzene when the ratio of silyllithium reagent to ether was 1:1. When the ratio was increased to 2:1, one methyl group was cleaved to the extent of 37.0 % and the second to the extent of 15.2 %.

The reaction of (I) with 1-methoxynaphthalene and 2-methoxynaphthalene gave the corresponding cleavage products quite readily. Apparently the cleavage is not affected noticeably by steric conditions of the aryl group. The reactions with the naphthyl ethers appeared to proceed more rapidly than with anisole.

Triphenylsilyllithium (I) reacted exclusively with the chloro group of *p*-chloroanisole to give hexaphenyldisilane (III) and *p*-anisyltriphenylsilane (IV).

$$(I) + p\text{-}ClC_6H_4OCH_3 \longrightarrow \underset{(III)}{(C_6H_5)_3SiSi(C_6H_5)_3} + \underset{(IV)}{(C_6H_5)_3SiC_6H_4OCH_3\text{-}p}$$

Reaction with *p*-fluoroanisole occurred at both groups, but cleavage was the predominant reaction. The result is in line with the lesser reactivity of fluoro- as compared to chlorobenzene.

$$(I) + p\text{-}FC_6H_4OCH_3 \rightarrow \underset{(II)}{(C_6H_5)_3SiCH_3} + p\text{-}FC_6H_4OH + \underset{(III)}{(C_6H_5)_3SiSi(C_6H_5)_3} + \underset{(IV)}{(C_6H_5)_3SiC_6H_4CCH_3\text{-}p}$$

Since steric requirements appeared to play such an important role in the reaction, it was thought that the use of a less bulky silylmetallic reagent might effect a cleavage more readily. This was partially confirmed by a 3.57% yield of phenol obtained from the reaction of dimethylphenylsilyllithium (V) with phenetole, a reaction which did not take place with (I). However, the reaction of (V) with 2-methoxynaphthalene did not proceed more readily than when (I) was employed. In fact, a lower yield of trimethylphenylsilane was obtained, probably due to the increased difficulty in the isolation procedure.

The reaction of triphenylsilyllithium with thioanisole, the sulfur analog of anisole, gave methyltriphenylsilane (II), hexaphenyldisilane (III) and tetraphenylsilane (VI). It would seem that, in addition to the usual displacement, another reaction mechanism

$$(I) + C_6H_5SCH_3 \longrightarrow \underset{(II)}{(C_6H_5)_3SiCH_3} + \underset{(III)}{(C_6H_5)_3SiSi(C_6H_5)_3} + \underset{(VI)}{(C_6H_5)_4Si}$$

must be considered. The mechanism is probably similar to one proposed for the reaction of triphenylsilyllithium (I) with diphenyl sulfide[9]. Such a mechanism would involve the initial formation of triphenyl(phenylthio)silane. The thiosilane would subsequently be cleaved by excess triphenylsilyllithium present with formation of the observed hexaphenyldisilane.

EXPERIMENTAL

All melting points are uncorrected. Reactions were carried out under an atmosphere of dry, oxygen-free nitrogen. Tetrahydrofuran was freed from peroxides and moisture before use by refluxing over sodium, followed by distillation from lithium aluminum hydride.

Triphenylsilyllithium and anisole

A tetrahydrofuran solution of 0.059 mole of triphenylsilyllithium[10] was added slowly to 6.40 g (0.059 mole) of anisole dissolved in 120 ml of tetrahydrofuran. There was no apparent reaction during the addition, which was completed in 45 min. The color of the solution was dark brown. The reaction mixture was warmed at 50° for 24 h, at which time Color Test I[11] was slightly positive. Hydrolysis was effected with concentrated aqueous ammonium chloride solution, and the organic layer separated.

The organic layer was extracted several times with a total of 400 ml of 2.5% aqueous sodium hydroxide. The basic extract was subsequently acidified with 10% aqueous hydrochloric acid, and the acidified solution was extracted with ether. The ether extracts were dried over sodium sulfate and later evaporated under an air-jet to leave an oil with a strong phenolic odor. This was brominated following a published procedure[12], and the resulting solid was recrystallized from ethanol–water to give 7.75 g (31.5%) of 2,4,6-tribromophenol, m.p. 93.5–94° (mixture melting point).

The original organic layer was evaporated to leave a white solid which was chromatographed on alumina. Elution of the column with petroleum ether (b.p. 60–70°) gave a white solid which was recrystallized from ethanol to yield 10.4 g (64.2 %) of methyltriphenylsilane, m.p. 67–69° (mixture melting point, infrared spectrum). Elution of the column with benzene gave a trace of impure tetraphenylsilane, melting range 172–220°, identified by comparison of the infrared spectrum with that of an authentic sample. Further elution of the column with ethyl acetate and with ethanol gave a mixture of triphenylsilanol and 4-hydroxybutyltriphenylsilane which could not be separated, 0.60 g (~ 3.70 %), 120–145° melting range (infrared spectrum).

Triphenylsilyllithium and phenetole (attempted)

To 2.71 g (0.059 mole) of freshly distilled phenetole dissolved in 25 ml of tetrahydrofuran was added a tetrahydrofuran solution of 0.059 mole of triphenylsilyllithium. The reaction mixture was warmed at 50° for 24 h. Color Test I was strongly positive. The reaction mixture was then stirred at 60° for 72 h, at which time Color Test I was only moderately positive. The dark red solution was hydrolyzed with ammonium chloride solution and worked up in the same manner as described in the previous reaction. The basic extraction gave a small amount of an oily residue with a strong phenolic odor. This was derivatized with bromine as in the previous experiment to give a small amount of light brown solid melting over the range 75–95°. A recrystallization from ethanol–water raised the melting point to 83–90°; however, there was not enough material for a second recrystallization.

Evaporation of the ether from the original organic layer left a white, oily solid which was chromatographed on alumina as in the previous reaction. The first fraction was an oil which was distilled at reduced pressure to give 6.45 g (9.46%) of triphenylsilane, b.p. 140–145° (0.5 mm) (infrared spectrum comparison). From the vacuum pump trap was removed 0.60 g (8.33%) of recovered phenetole (infrared spectrum). The second fraction from the chromatography was 0.65 g (3.28%) of tetraphenylsilane (infrared spectrum). The third fraction, eluted by ethyl acetate, was 6.00 g (30.6 %) of 4-hydroxybutyltriphenylsilane, m.p. 109–111° (mixture melting point). The last fraction, eluted by ethanol, was 0.25 g (1.53%) of triphenylsilanol (mixture melting point identification).

Triphenylsilyllithium and phenyl n-propyl ether (attempted)

To 6.81 g (0.05 mole) of phenyl *n*-propyl ether dissolved in 50 ml of tetrahydrofuran was added 0.05 mole of triphenylsilyllithium in tetrahydrofuran solution. Color Test I was strongly positive upon the completion of addition. The reaction mixture was warmed at 50° for 72 h, but Color Test I was still positive. Hydrolysis was effected with concentrated ammonium chloride solution, and basic extraction work-up employed.

Evaporation of the organic layer left a yellow oil which was chromatographed on alumina in the usual manner. The first fraction was an oil which was distilled at reduced pressure to give 6.10 g (33.9 %) of triphenylsilane, b.p. 141–145° (0.5 mm) (infrared spectrum). The oil crystallized when cooled in an ice-bath. The solid was recrystallized from methanol to give triphenylsilane as white crystals, m.p. 45–46.5° (mixture melting point). The other materials from the chromatography were 0.30 g (1.78%) of tetraphenylsilane, 3.40 g (~ 24.6%) of a mixture of triphenylsilanol and

4-hydroxybutyltriphenylsilane, and 0.10 g (0.73%) of pure triphenylsilanol. All of the compounds were identified by mixture melting points and/or infrared spectra comparisons.

Evaporation of the solvent from the basic extraction failed to leave a trace of phenolic material.

Triphenylsilyllithium and p-dimethoxybenzene

A. 1:1 Ratio. A tetrahydrofuran solution of 0.059 mole of triphenylsilyllithium was added to 8.15 g (0.059 mole) of *p*-dimethoxybenzene dissolved in 30 ml of tetrahydrofuran. The solution was heated at 50°. Color Test I was green after 6 h, but was negative after 12 h. The solution was hydrolyzed with concentrated ammonium chloride solution and the usual basic extraction work-up employed.

Evaporation of the solvent from the original organic layer left a white solid, which was chromatographed on alumina using the same procedure as described in the first reaction. There was obtained 9.80 g (60.5%) of methyltriphenylsilane, m.p. 67–69° (mixture melting point) and 0.70 g ($\sim$ 4.60%) of a mixture of triphenylsilanol and 4-hydroxybutyltriphenylsilane (infrared spectrum), melting range 128–138°.

Evaporation of the ether from the basic extract fraction left 4.30 g of a very dark red-brown solid. This was extracted with hot petroleum ether (b.p. 80–110°) to give, upon cooling, 2.20 g (30.2%) of hydroquinone monomethyl ether, m.p. 55–57° (mixture melting point, infrared spectrum).

B. 2:1 Ratio. To 5.00 g (0.036 mole) of *p*-dimethoxybenzene dissolved in 50 ml of tetrahydrofuran was added 0.072 mole of triphenylsilyllithium in tetrahydrofuran solution. The reaction mixture was warmed at 50°. After 24 h, Color Test I was moderately positive. Hydrolysis was effected with concentrated ammonium chloride solution, and the usual work-up with basic extraction was employed.

Evaporation of the ether from the original organic layer left a white solid which was chromatographed on alumina in the usual manner. Methyltriphenylsilane, 11.5 g (116% based on the availability of one methoxyl or 57.8% on two available methoxyl groups), m.p. 67–69° (mixture melting point); tetraphenylsilane, 0.10 g (0.40%) (infrared spectrum); and the usual mixture of triphenylsilanol and 4-hydroxybutyltriphenylsilane, 0.45 g ($\sim$ 2.27%) (infrared spectrum), were isolated.

The ether from the basic extracts was evaporated to leave 4.20 g of a dark-brown solid. The solid was extracted several times with hot petroleum ether (b.p. 60–70°) which upon cooling gave 1.65 g (37.0%) of hydroquinone monomethyl ether, m.p. 56–58° (mixture melting point, infrared spectrum). The remaining residue was extracted several times with hot benzene. Upon cooling, 0.60 g (15.2%) of hydroquinone, m.p. 170–172° (mixture melting point), crystallized.

Triphenylsilyllithium and 1-methoxynaphthalene

To 7.91 g (0.05 mole) of 1-methoxynaphthalene dissolved in 50 ml of tetrahydrofuran was added 0.05 mole of triphenylsilyllithium in tetrahydrofuran solution. After warming at 50° for 3 h, the solution gave a moderate Color Test I; after 8 h, faintly positive; and after 10 h, negative. The deep red solution was hydrolyzed with concentrated ammonium chloride solution, and the usual basic extraction work-up was carried out.

The yellow solid resulting from evaporation of the solvent from the original organic layer was chromatographed on alumina. The products obtained were 6.65 g

(48.5%) of methyltriphenylsilane, 0.90 g (11.4%) of recovered 1-methoxynaphthalene; and 0.25 g (~ 1.81%) of a mixture of triphenylsilanol and 4-hydroxybutyltriphenylsilane. All products were identified by mixture melting points or comparison of the infrared spectra.

Evaporation of the ether from the basic extraction left 4.40 g (60.8%) of crude 1-naphthol as a red solid, m.p. 92–96°. This was recrystallized from petroleum ether (b.p. 80–110°) to give 4.20 g (58.2%) of white flakes, m.p. 93–95° (mixture melting point, infrared spectrum).

Triphenylsilyllithium and 2-methoxynaphthalene

2-Methoxynaphthalene, 7.91 g (0.05 mole), was dissolved in 50 ml of tetrahydrofuran, and a tetrahydrofuran solution of 0.05 mole of triphenylsilyllithium was added. The reaction mixture was warmed at 50°. Color Test I was positive after 6 h, but after 16 h, it was negative. The solution was hydrolyzed with concentrated ammonium chloride solution, and the hydrolyzed mixture was worked up with the usual basic extraction.

The yellow solid resulting from evaporation of the solvent from the original organic layer was chromatographed on alumina. From the chromatography were isolated 7.25 g (52.5%) of methyltriphenylsilane, m.p. 67–69°; 0.30 g (3.78%) of recovered 2-methoxynaphthalene, m.p. 71.5–75° from petroleum ether (b.p. 60–70°); 0.10 g (0.59%) of tetraphenylsilane; and the usual mixture of silanol and hydroxy compound. The products were identified by the method of mixture melting points.

Evaporation of the solvent from the basic extraction left a brown solid which was recrystallized several times from petroleum ether (b.p. 80–110°) to give 4.25 g (58.8%) of 2-naphthol, m.p. 119–122° (mixture melting point, infrared spectrum).

Triphenylsilyllithium and p-chloroanisole

A tetrahydrofuran solution of triphenylsilyllithium (0.05 mole) was added slowly to 7.13 g (0.05 mole) of *p*-chloroanisole dissolved in 50 ml of tetrahydrofuran. Color Test I was positive at the completion of addition, but was negative after the reaction mixture had been warmed at 50° for 2 h. The brown reaction mixture was hydrolyzed with concentrated ammonium chloride solution. A suspended white solid was filtered off, washed with ether, and dried to give 5.30 g (40.7%) of hexaphenyldisilane, m.p. 363–364° (mixture melting point). The organic layer was worked up in the same manner as described previously.

Evaporation of the original organic solution left a white solid which was chromatographed on alumina to give 0.90 g (12.6%) of recovered *p*-chloroanisole (infrared spectrum); 1.08 g (5.73%) of *p*-anisyltriphenylsilane, m.p. 157–159° after recrystallization from petroleum ether (b.p. 60–70°) (mixture melting point, infrared spectrum); and the usual impure triphenylsilanol, 0.90 g (~ 6.50%) (infrared spectrum).

Evaporation of the basic extraction left only a trace of a dark oil with a phenolic odor, which could not be identified.

Triphenylsilyllithium and p-fluoroanisole

To 6.30 g (0.05 mole) of *p*-fluoroanisole dissolved in 50 ml of tetrahydrofuran was added 0.05 mole of triphenylsilyllithium in tetrahydrofuran solution. The reaction mixture was warmed at 50°. After 1 h, Color Test I was strongly positive; after 8 h, it was only faintly positive. After 24 h, the color test was negative, and the gray solution was hydrolyzed and worked up following the usual procedure.

Evaporation of the ether from the original organic layer left a yellow solid which was chromatographed on alumina. There were obtained 6.75 g (49.2 %) of methyltriphenylsilane, m.p. 67–69° (mixture melting point); and 0.20 g (1.09 %) of *p*-anisyltriphenylsilane, m.p. 160–161.5° (mixture melting point).

Evaporation of the ether from the basic extraction left a brown oil with a strong phenolic odor. This was distilled at reduced pressure to give 1.90 g (30.5 %) of *p*-fluorophenol, b.p. 76–77° (15 mm), n_D^{20} 1.5055, m.p. 24.5° (lit. value[13], b.p. 87°/23 mm, m.p. 26.5–27.0°). The infrared spectrum showed an associated OH, $=$C–F split at 8.20 and 8.35 μ, *p*-disubstitution at 12.10 μ, and an aromatic substitution band at 13.40 μ.

Dimethylphenylsilyllithium and 2-methoxynaphthalene

To 15.8 g (0.10 mole) of 2-methoxynaphthalene disolved in 50 ml of tetrahydrofuran was added a tetrahydrofuran solution of dimethylphenylsilyllithium[10] prepared by the lithium cleavage of 13.5 g (0.05 mole) of *sym*-tetramethyldiphenyldisilane in tetrahydrofuran solution. The reaction mixture gave a positive Color Test I after it had been warmed at 50° for 24 h. The solution was hydrolyzed with aqueous ammonium chloride and the usual basic extraction work-up effected.

The original organic solution was distilled to remove the solvents, and the resulting yellow oil was distilled at atmospheric pressure to give 5.40 g (35.9 %) of impure trimethylphenylsilane, boiling range 140–170°, n_D^{20} 1.4948 (lit. value[14], b.p. 166–167°/735 mm, n_D^{20} 1.4896). The oil was redistilled at atmospheric pressure to give 3.70 g (24.6 %) of material, boiling range 157–162°, n_D^{20} 1.4928. The infrared spectrum of the oil as a capillary cell was superimposible with that of an authentic sample.

Evaporation of the ether from the original basic extracts left 6.90 g (47.8 %) of crude 2-naphthol, m.p. 115–120°. Several recrystallizations from petroleum ether (b.p. 80–110°) gave 4.95 g (34.4 %) of pure 2-naphthol, m.p. 121–122° (mixture melting point, infrared spectrum).

Dimethylphenylsilyllithium and phenetole

A tetrahydrofuran solution of dimethylphenylsilyllithium, prepared by the lithium cleavage of 10.0 g (0.037 mole) of *sym*-tetramethyldiphenyldisilane, was added to 9.17 g (0.075 mole) of phenetole dissolved in 50 ml of tetrahydrofuran. The reaction mixture was warmed at 50°, Color Test I being taken at various intervals. After 72 h, the color test was still strongly positive. The usual basic extraction work-up was carried out following aqueous ammonium chloride hydrolysis of the reaction mixture.

The original organic layer was distilled at atmospheric pressure to give, subsequent to removal of the solvent, 10.2 g of impure phenetole, boiling over the range 151–160° (740 mm), n_D^{20} 1.5062. This was redistilled to give 7.70 g (84.0 %) of recovered phenetole, b.p. 167–170° (760 mm), n_D^{20} 1.5066 (starting material, b.p. 172°, n_D^{20} 1.5076). The infrared spectrum was superimposable with that of the starting material. Ethyldimethylphenylsilane, the cleavage product, could not be detected.

Evaporation of the ether from the original basic extraction left a small amount of a brown oil with a strong phenolic door. This was brominated to give 0.88 g (3.57 %) of crude 2,4,6-tribromophenol, m.p. 87–91°. Several recrystallizations from ethanol-water raised the melting point to 93–94° (mixture melting point).

Triphenylsilyllithium and thioanisole

Triphenylsilyllithium, 0.05 mole in tetrahydrofuran solution, was added to 6.20 g (0.05 mole) of thioanisole dissolved in 50 ml of tetrahydrofuran. The addition was completed in 40 min, and the resulting dark solution gave a positive Color Test I. The reaction mixture was warmed at 50° for 24 h, at which time the color test was negative. The solution was hydrolyzed with concentrated ammonium chloride solution. A suspended white solid was filtered off to give 2.60 g of white solid, 224–304° melting range. The solid was extracted with hot ethyl acetate to leave 0.80 g (6.17 %) of hexaphenyldisilane, m.p. 364–368° (mixture melting point). From the chilled ethyl acetate crystallized 1.40 g (8.33 %) of tetraphenylsilane, m.p. 232–234° (mixture melting point). The organic layer from the hydrolysis was subjected to the usual basic extraction work-up.

Subsequent to evaporation of the solvent, the resulting yellow solid was chromatographed on alumina to give 1.80 g (13.1 %) of methyltriphenylsilane, m.p. 65.5–67° (mixture melting point, infrared spectrum); and 0.90 g (5.35 %) of tetraphenylsilane, m.p. 231–233° (mixture melting point).

Evaporation of the ether from the basic extract failed to leave any material which might be taken for thiophenol.

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SUMMARY

The reaction of triphenylsilyllithium with some methyl aryl ethers gave methyltriphenylsilane and the corresponding phenolic compound. The mild cleavage could not be extended to the ethyl or *n*-propyl phenyl ethers. The extreme steric sensitivity of triphenylsilyllithium is considered to be the major factor contributing to the lack of cleavage, while steric requirements of the aryl group do not appear to affect the reaction. The cleavage was not facilitated by the use of less bulky silylmetallic reagents.

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