Utilization of Tetrabutylammonium Triphenyldifluorosilicate as a Fluoride Source for Silicon−Carbon Bond Cleavage†

Anthony S. Pilcher and Philip DeShong*

Department of Chemistry and Biochemistry, University of Maryland, College Park, Maryland 20742

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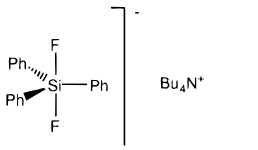
Tetrabutylammonium triphenyldifluorosilicate (TBAT) can be employed as a fluoride source to cleave silicon−carbon bonds thus generating *in situ* carbanions that coupled with a variety of electrophiles, including aldehydes and ketones, in moderate to high yields. Among the examples reported is the first instance of fluoride-induced intermolecular coupling between allyltrimethylsilane and imine derivatives. Also, of particular note is the TBAT-initiated coupling of primary alkyl halides with allyltrimethylsilane. TBAT is an easily handled crystalline solid that has several advantages over tetrabutylammonium fluoride (TBAF) as a fluoride source; it is anhydrous, nonhygroscopic, soluble in most commonly used organic solvents, and less basic than TBAF.

Carbon−carbon bond formation is often considered the most difficult challenge in synthetic organic chemistry, and new or improved solutions to carbon−carbon bond-forming reactions are continuously being sought. One of the most useful categories of reagents for this purpose is the organometallic carbon nucleophiles, including organolithium, organomagnesium, and organocopper compounds.[1] Unfortunately, these reagents do have limitations. Since they are extremely strong bases as well as potent nucleophiles, their use with base sensitive substrates is precluded. Organolithium and -magnesium reagents are incompatible with halo, nitro, and cyano functionalities. Finally, benzylic and allylic organometallics are notoriously difficult to generate and prone to homocoupling.[1]

An alternative methodology that circumvents these limitations is the generation of stabilized carbanions or carbanoids by cleavage of silicon−carbon bonds using fluoride anion.[2] The most commonly used fluoride source for this purpose is tetrabutylammonium fluoride (TBAF). In a recent article, we demonstrated the superiority of tetrabutylammonium triphenyldifluorosilicate (TBAT) to TBAF as a fluoride source for nucleophilic fluorination.[3] In this paper, we demonstrate that TBAT is useful for cleaving Si−C bonds to initiate carbon−carbon bond formation *via* coupling with a wide variety of electrophilic components, including aldehydes, ketones, imines, and primary alkyl halides in moderate to high yields. Among the examples is the first instance of intermolecular coupling between allyltrimethylsilane and an imine. Also of particular note is the TBAT-induced condensation of allyltrimethylsilane with primary alkyl halides.[4]

TBAT is an easily handled crystalline solid that has several advantages over tetrabutylammonium fluoride



Tetrabutylammonium triphenyldifluorosilicate
TBAT (1)

(TBAF) as a fluoride source: it is anhydrous, nonhygroscopic, and soluble in most commonly used organic solvents (THF, toluene, acetonitrile) and solutions of TBAT in these solvents are significantly less basic than the corresponding TBAF solutions. The fact that commercially available solutions of TBAF contain 2−3 equiv of water is also a severe limitation because a proton source is detrimental to reactions involving carbanions. Although various methods have been proposed for drying TBAF without accompanying decomposition, no procedure has become widely accepted for dehydrating this reagent.[5] On the other hand, anhydrous solutions of TBAT in THF, toluene, or acetonitrile are readily prepared.

TBAT-catalyzed cleavage of carbon−silicon bonds was a facile process in those cases involving allyl-, benzyl-, and alkynylsilane derivatives. In Table 1, the results of TBAT-generated carbanion additions to a variety of electrophiles are summarized. TBAT acts as a catalyst in these reactions, and the products obtained are TMS ethers.[6] Standard reaction conditions employed 2 equiv of the TMS compound and 0.1 equiv of TBAT; however, with enolizable substrates, it was observed that the yield of the adduct was increased by using a large excess of allyltrimethylsilane (10 equiv) and 1 equiv of TBAT.

Entries 1−6 involve the reaction of stabilized carbanions with benzaldehyde and are listed in the order of decreasing relative carbanion stability. Note that increasing temperatures are required to cleave the carbon−silicon bond as the pK_a of the conjugate acid increases. The reactions in entries 1−4 gave high yields of the desired product. TBAT, however, was unable to promote condensation with arylsilane or vinylsilane derivatives

† Dedicated to Richard W. Franck on the occasion of his 60th birthday.

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(3) Pilcher, A. S.; Ammon, H. L.; DeShong, P. *J. Am Chem. Soc.* **1995**, *117*, 5166.

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(5) Cox, D. P.; Terpinsky, J.; Lawrynowicz, W. *J. Org. Chem.* **1984**, *49*, 3216.

(6) Some of the TMS ethers resulting from condensation are hydrolytically unstable. For these products, the standard workup procedures involving exposure of the crude products to dilute acid resulted in removal of the TMS ether.

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Table 1. Coupling of TBAT-Generated Carbanions with Electrophiles

Entry	Reaction Equation	% Yield[a]
1	Ph—≡—TMS (**2**) + Ph(C=O)H (**3**) → TBAT (0.1equiv), THF, 0° C, 20 min → Ph(OH)C≡C—Ph (**4**)	81
2	2-TMS-1,3-dithiane (**5**) + **3** → TBAT (0.1 equiv), THF, 27° C, 15 min → Ph(OTMS)-2-dithiane (**6**)	96
3	Ph(TMS)CH₂ (**7**) + **3** → TBAT (0.1 equiv), THF, 70° C, 10 min → Ph(OTMS)CH(Ph)CH₂ (**8**)	93
4	allyl-TMS (**9**) + **3** → TBAT (0.1 equiv), THF, 70° C, 10 min → Ph(OH)CH(CH₂CH=CH₂) (**10**)	92
5	Ph—TMS (**11**) + **3** → TBAT (2 equiv), dioxane, 110° C, 48 h → no reaction	0
6	vinyl-TMS (**12**) + **3** → TBAT (2 equiv), dioxane, 110° C, 48 h → no reaction	0
7	**9** + C_5H_{11}(C=O)H (**13**) → TBAT (1 equiv), THF, 70° C, 10 min → C_5H_{11}(OH)CH(CH₂CH=CH₂) (**14**)	64[b]
8	**9** + Ph(CH)(C=O)H (**15**) → TBAT (1 equiv), THF, 70° C, 4.5 h → Ph(OH)CH(CH₂CH=CH₂) (**16**)	73[c]
9	**9** + Ph(C=O)CH₃ (**17**) → TBAT (1 equiv), THF, 70° C, 40 min → Ph(OH)C(CH₃)(CH₂CH=CH₂) (**18**)	88
10	**9** + cyclohexanone (**19**) → TBAT (1 equiv), THF, 70° C, 24 h → 1-OTMS-1-allylcyclohexane (**20**)	96[b]
11	**9** + cyclopentanone (**21**) → TBAT (1 equiv), THF, 70° C, 20 min → 1-OTMS-1-allylcyclopentane (**22**)	37[b]
12	**9** + Ph(N=Ph)CH (**23**) → TBAT (2 equiv), THF, 70° C, 30 h → Ph(HN-Ph)CH(CH₂CH=CH₂) (**24**)	79
13	**9** + Ph(N=Ph)CH (**25**) → TBAT (2 equiv), THF, 70° C, 30 h → Ph(HN-Ph)CH(CH₂CH=CH₂) (**26**)	58
14	**9** + Ph(N=propyl)CH (**27**) → TBAT (2 equiv), THF, 70° C, 30 h → no reaction	0
15	**9** + C_6H_{13}-epoxide (**28**) → TBAT (2 equiv), dioxane, 110° C, 48 h → no reaction	0

a) Yields represent purified material unless noted otherwise. b) Yield determined by GC. c) Erythro:threo = 85:15.

(entries 5 and 6), even under forcing reaction conditions. Apparently, the pK_a values of benzene and ethylene are too high for effective desilylation.

In entries 7−11 of Table 1, the results of the coupling of allyltrimethylsilane with various carbonyl compounds are reported. Hexanal (entry 7) gave only a moderate yield of the homoallyl alcohol product due to the competing aldol condensation of the aldehyde. A control experiment with hexanal demonstrated that the aldol condensation was catalyzed by the alkoxide generated when allyl anion adds to the carbonyl and was not the result of fluoride-induced self-condensation.[6,7] Previous studies by Sakurai had demonstrated that TBAF will also catalyze couplings between allylsilane derivatives and carbonyl compounds.[8]

Addition of allyltrimethylsilane to an aldehyde bearing an α-stereogenic center (entry 8) occurred with moderate selectivity to provide an 85:15 erythro:threo mixture of homoallyl alcohols.[9] The allylation reaction was also effective for acetophenone (entry 9) and cyclohexanone (entry 10), but with cyclopentanone (entry 11), aldol condensation was the dominant pathway.

Fluoride-catalyzed condensation of imines and allytrimethylsilane is an unprecedented reaction.[10] Previously, allyl boronates and stannanes have been shown to react with imine derivatives under Lewis acid-catalyzed conditions.[11] Also, Overman, Speckamp, and Livinghouse have reported intramolecular additions of allylsilane analogs to iminium salts.[12,13] However, neither the inter- nor intramolecular fluoride-induced condensation of an imine with allyltrimethylsilane has been reported. *N*-Benzylideneaniline may also be allylated by this methodology to give the secondary amine (entry 12) in excellent yield, although this reaction is not catalytic in the silicate salt, TBAT. *N*-Benzylidenebenzylamine underwent condensation though the yield was reduced somewhat (58%). Allylation did not occur with *N*-benzylidenepropylamine (entry 14) presumably because the imine was not sufficiently electrophilic. The scope and limitations of fluoride-catalyzed condensation of imines with allylsilanes will be reported in due course.

Epoxides are not sufficiently electrophilic to take part in this reaction, even under forcing conditions (entry 15).

The major advantage of using TBAT rather than TBAF in these experiments is that because the reaction conditions are virtually neutral, one avoids problems arising from the strongly basic conditions involved in TBAF

(7) In a control experiment, treatment of hexanal with TBAT under the described conditions in the absence of allyltrimethylsilane did not produce aldol products.

(8) (a) Hosomi, A.; Shirahata, A.; Sakurai, H. *Tetrahedron Lett.* **1978**, 3043. (b) Sakurai, H. *Pure App. Chem.* **1982**, *54*, 1. (c) Sakurai, H.; Hosomi, A.; Saito, M. Sasaki, K.; Iguchi, H.; Sasaki, J.; Araki, Y. *Tetrahedron* **1983**, *39*, 883 and references cited therein. (d) Sakurai has also reported the fluoride-catalyzed condensation of crotyltrifluorosilane derivatives with aldehydes: Kira, M.; Kobayashi, M.; Sakurai, H. *Tetrahedron Lett.* **1987**, *28*, 4081. (e) Sakurai, H. *Synlett* **1990**, 1 and references cited therein.

(9) Assignment of relative configuration was based on (a) GC retention times: (Jones, P. R.; Goller, E. J.; Kauffman, W. J. *J. Org. Chem.* **1971**, *36*, 3311) and (b) ^{1}H NMR chemical shifts of the methyl group: (Guyon, R.; Villa, P. *Bull. Soc. Chim. Fr.* **1972**, 1375).

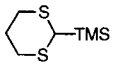
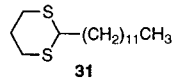
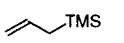
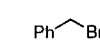
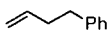
(10) This is the first example of fluoride-initiated intermolecular coupling between allyltrimethylsilane and an imine derivative. For an example of an alkoxide-induced reaction between an imine and a benzylsilane derivative, see: Shimizu, S.; Ogata, M. *Synth.Commun.* **1989**, *19*, 2219.

(11) (a) Chtara, R. A.; Moreau, J. L.; Gaudemar, M. *C. R. Acad. Sci., Ser. C* **1975**, *280*, 3115 and references cited therein. (b) Yamamoto, Y.; Ito, W.; Maruyama, K. *J. Chem. Soc., Chem. Commun.* **1985**, 1131 and references cited therein. (c) Keck, G. E.; Enholm, E. J. *J. Org. Chem.* **1985**, *50*, 146. (d) Wuts, P. G. M.; Jung, Y. W. *Tetrahedron Lett.* **1986**, *27*, 2079. (e) Yamamoto, Y. *Alrichimica Acta* **1987**, *20*, 45 and references cited therein. (f) Hoffmann, R. W.; Endesfelder, A. *Liebigs Ann. Chem.* **1987**, 215 and references cited therein. (g) Ciufolini, M. A.; Spencer, G. O. *J. Org. Chem.* **1989**, *54*, 4739.

(12) (a) Heerding, D. A.; Hong, C. Y.; Kado, N.; Overman, L. E. *J. Am. Chem. Soc.* **1993**, *115*, 11028 and references cited therein. (b) Hiemstra, H.; Sno, M. H. A. M.; Vijn, R. J.; Speckamp, W. N. *J. Org. Chem.* **1985**, *50*, 4014 and references cited therein. (c) Kercher, T.; Livinghouse, T. *J. Am. Chem. Soc.* **1996**, *118*, 4200.

(13) For an account of the reaction between imines and allenyl silanes, see: Jin, J.; Smith, D. T.; Weinreb, S. M. *J. Org. Chem.* **1995**, *60*, 5366. Borzilleri, R. M.; Weinreb, S. M.; Parzez, M. *J. Am Chem. Soc.* **1994,** *116*, 9789.

Table 2. Coupling of TBAT-Generated Carbanions with Alkyl Halides

Entry	Reaction Equation	% Yield[a]
1	Ph—≡—TMS (**2**) + $CH_3(CH_2)_{10}CH_2Br$ (**29**) → TBAT (2 equiv), THF, 50° C, 46 h → $PhCC(CH_2)_{11}CH_3$ (**30**)	81
2	 (**5**) + **29** → TBAT (2 equiv), THF, 50° C, 22 h →  (**31**)	52
3	 (**7**) + **29** → TBAT (2 equiv), THF, 70° C, 46 h → $PhCH_2(CH_2)_{11}CH_3$ (**32**)	84
	 (**9**) + $CH_3(CH_2)_{10}CH_2X$ → TBAT (2 equiv), THF, 70° C, 24 h → $CH_2{=}CH(CH_2)_{12}CH_3$ (**36**)	
4	**33**: X = Br	87
5	**34**: X = I	87
6	**35**: X = Cl	13
7	**9** +  (**37**) → TBAT (2 equiv), THF, 70° C, 12 h →  (**38**)	62
8	**9** + $CH_3(CH_2)_5CHBrCH_3$ (**39**) → TBAT (2 equiv), THF, 70° C, 24 h → $CH_3(CH_2)_5CH_2CH_3$ / $CH_2CH{=}CH_2$ (**40**)	27[b]
	9 + $CH_3(CH_2)_{10}CH_2X$ → TBAT (2 equiv), THF, 70° C, 24 h → no **36**	
9	**41**: X = OTs	no reaction
10	**42**: X = OMs	decomp.
11	**43**: X = OTf	decomp.

a) Isolated, pure product. b) Yield determined by GC.

reactions. For example, we have demonstrated that a large number of protecting groups are stable to the reaction conditions employed above.[14]

Primary alkyl halides can also be coupled with silane derivatives upon treatment with TBAT. As summarized in Table 2, these condensations were performed with either 5 (entries 1−3) or 10 equiv (entries 4−11) of the respective TMS reagent and 2 equiv of TBAT. By doubling the amount of the allyltrimethysilane reagent from 5 to 10 equiv, the reaction times were reduced significantly. Precise temperature control was critical in this coupling reaction because at temperatures above 70 °C increasing amounts of elimination products were observed.

Alkynyl and dithianyl reagents couple with 1-bromododecane to give alkylated products in good to moderate yields as expected on the basis of the stability of the anions generated by the *in situ* desilylation conditions. However, the efficient alkylation of benzyltrimethylsilane (**7**) and allyltrimethylsilane (**9**) (entries 3−5, Table 2) with primary halides was unexpected. With both of these silane derivatives, TBAT-induced alkylation gave a high yield of the corresponding homologated adducts **32** and **36**, respectively. TBAT is unique with regard to this alkylation system. Control experiments with TBAF resulted in decomposition of the substrates without formation of products. Schwesinger et al. had previously demonstrated that "naked fluoride" as the phosphazenium (PPN) salt was able to catalyze allylation of primary halides.[4a] However, the TBAT-based procedure outlined in Table 2 is superior to the PPN methodology in both yield of adduct and ease of preparation.

An investigation of the allylation reaction with various halide derivatives was also undertaken. This study demonstrated that allylation of iodoalkane **34** is comparable to the reaction with bromoalkane, while chloroalkane **35** reacted slowly and gave only 13% pentadecene (**36**) after 24 h. Benzyl bromide (**37**) was also smoothly allylated using the TBAT protocol (entry 7). The reaction was clean and faster than that with dodecyl bromide; however, the yield was only moderate due to loss of the volatile product during workup and purification. The displacement of a secondary bromide (entry 8) from 2-bromododecane (**39**) gave only 27% of the desired product, the remainder being dodecenes, the elimination product. Although the coupling reaction worked well with primary bromides and iodides, primary dodecyl sulfates could not be coupled with allyltrimethylsilane, suggesting that the reaction mechanism may have an electron transfer component (entries 9−11).[2b,15]

Alkylation of carbanions with alkyl halides is traditionally accomplished with organocuprate chemistry. Since the organocuprates are normally generated from the corresponding organolithium or organomagnesium species, they suffer the same limitations. In particular, benzyl- and allyllithium reagents are difficult to prepare due to their propensity to undergo homocoupling.[1] The TBAT-initiated methodology described above avoids this problem because the anion is generated *in situ* by desilylation.

The results of this study indicate that TBAT is an effective source of fluoride for silicon−carbon bond cleavage applications. Furthermore, we have shown that the carbanions generated by this technology can be coupled

(14) Unpublished results, A. S. Pilcher, P. Loeszos, J. W. Schwantes, V. Lee, and A. L. Slover.
(15) Ashby, E. C.; DePriest, R. N. *Tetrahedron Lett.* **1982**, *23*, 5251.

with aldehydes, ketones, imines, and alkyl halides in good yields. Further applications of this technology to synthesis of biologically active substances will be reported in due course.

Experimental Section

General Experimental. Flash column chromatography was performed using thick-walled glass columns and "medium-pressure" silica (230−400 mesh, Merck). All solvents were distilled from calcium chloride prior to use unless noted otherwise. Tetrahydrofuran (THF) was distilled from sodium/benzophenone ketyl. All reagents were distilled, recrystallized, or chromatographed prior to use unless otherwise noted.

Gas chromatography was performed using a gas chromatograph equipped with a flame ionization detector and a 25-m capillary column coated with cross-linked methyl silicone. All compounds for which elemental analysis was not obtained were >95% pure as judged by gas chromatographic and NMR spectral analysis. ^{1}H and/or ^{13}C NMR spectra of these substances are included in the supporting information.

Carbanion Addition to Aldehydes and Ketones. For nonenolizable substrates, 0.1 equiv of TBAT and 2 equiv of the TMS reagent were used. For enolizable substrates, 1 equiv of TBAT and 10 equiv of the reagent were used to promote the carbanion addition pathway over the aldol condensation pathway. Reactions were followed by GC, and the following two examples are illustrative.

Synthesis of 4-Phenyl-4-hydroxy-1-butene (10) [936-58-3]. (All Registry numbers supplied by authors.) Benzaldehyde (102 μL, 1.00 mmol), allyltrimethylsilane (318 μL, 2.00 mmol), and tetrabutylammonium triphenyldifluorosilicate (TBAT, 54 mg, 0.10 mmol) were dissolved in THF (5 mL). The clear, colorless solution was heated in a 70 °C oil bath under N_2. After 5 min, the solution had changed to yellow, and after 10 min, the reaction was complete. The THF and excess allyltrimethylsilane were removed at reduced pressure. The concentrate was redissolved in 30 mL of Et_2O and washed with 1 M HCl (30 mL, stirred until the TMS group was completely hydrolyzed as determined by GC), water (30 mL), and 5% $NaHCO_3$ (30 mL), then dried ($MgSO_4$), and concentrated at reduced pressure. The crude alcohol was flash column chromatographed (hexanes/Et_2O) to give 139 mg (93%) of homoallylic alcohol **10** as a clear, colorless oil (99% pure by GC): IR (CCl_4) 3619 (s), 3067 (m), 2913 (m), 1639 (m), 1042 (s); ^{1}H NMR ($CDCl_3$) 7.34 (5H, m), 5.82 (1H, m), 5.16 (2H, m), 4.72 (1H, t, 7), 2.50 (2H, m), 2.15 (1H, bs); ^{13}C NMR ($CDCl_3$) 143.8, 134.4, 128.3, 127.4, 125.8, 118.2, 73.3, 43.7.

Synthesis of 4-Phenyl-4-hydroxy-1-pentene (18) [4743-74-2]. Acetophenone (238 mL, 2.00 mmol), allyltrimethylsilane (3.18 mL, 20 mmol), and TBAT (1.08 g, 2.00 mmol) were dissolved in THF (10 mL). The clear, colorless solution was heated in a 70 °C oil bath under N_2. After 4 min, the solution turned orange, and after 40 min, the reaction was complete. The THF and excess allyltrimethylsilane were removed at reduced pressure. The concentrate was redissolved in 50 mL of 50/50 Et_2O/EtOAc, then chilled to 5 °C, and filtered to remove any excess TBAT. The filtrate was washed with 1 M HCl (50 mL, stirred until the TMS group was completely hydrolyzed as determined by GC), water (2 × 50 mL), and 5% $NaHCO_3$ (50 mL), then dried ($MgSO_4$), and concentrated at reduced pressure. The crude alcohol was flash column chromatographed (hexanes/Et_2O gradient) to give 293 mg (88%) of homoallylic alcohol **18** as a clear, colorless oil (98% pure by GC): IR (CCl_4) 3606 (m), 3568 (m), 3082 (m), 2982 (vs), 1641 (m), 1602 (m), 1448 (vs), 1071 (vs), 1001 (vs), 928 (vs), 916 (vs), 866 (m); ^{1}H NMR ($CDCl_3$) 7.43 (2H, m), 7.34 (2H, m), 7.23 (1H, m), 5.62 (1H, m), 5.12 (2H, m), 2.68 (1H, dd, 14 and 6), 2.50 (1H, dd, 14 and 8), 2.08 (1H, s), 1.55 (3H, s); ^{13}C NMR ($CDCl_3$) 147.6, 133.6, 128.1, 126.6, 124.7, 119.3, 73.6, 48.4, 29.8.

α-Hydroxy-1-benzyl-2-phenylacetylene (4) [1817-49-8]. This reaction was done on a 2.00 mmol scale and the crude product was purified by flash column chromatography (hexanes/CH_2Cl_2 gradient) to give 338 mg of the propargyl alcohol as a yellow oil (98% pure by GC, 81% yield): IR (CCl_4) 3603 (s), 3067 (m), 3035 (m), 2233 (w), 2204 (w), 1031 (vs); ^{1}H NMR ($CDCl_3$) 7.40 (10H, m), 5.69 (1H, d, 6), 2.41 (1H, d, 6); ^{13}C NMR ($CDCl_3$) 140.6, 133.1, 131.7, 128.7, 128.6, 128.4, 128.3, 126.7, 88.7, 86.7, 65.1.

α-(2-(1,3-Dithianyl))-α-(trimethylsiloxy)methylbenzene (6). This reaction was done on a 2.00 mmol scale, and the crude product was purified by flash column chromatography (hexanes/Et_2O gradient) to give 576 mg of the trimethylsilyl ether as a clear, colorless oil (>99% pure by GC, 96% yield): IR (CCl_4) 3090 (w), 2958 (s), 2900 (s), 1425 (m), 1252 (vs), 1088 (vs), 1072 (vs), 890 (vs), 845 (vs); ^{1}H NMR ($CDCl_3$) 7.34 (5H, m), 4.76 (1H, d, 7), 4.28 (1H, d, 7), 2.80 (4H, m), 2.03 (1H, m), 1.86 (1H, m); ^{13}C NMR ($CDCl_3$) 141.3, 128.0, 127.9, 126.6, 77.6, 54.7, 30.0, 29.8, 25.7, 0.2.

***β*-Phenyl-α-(trimethylsiloxy)ethylbenzene (8) [18044-11-6].** This reaction was done on a 5.00 mmol scale, and the crude product was purified by flash column chromatography (hexanes) to give 1.33 g of the trimethylsilyl ether as a clear, colorless oil (95% pure by GC, 93% yield): IR (CCl_4) 3030 (s), 2957 (s), 1604 (m), 1251 (vs), 1094 (vs), 1069 (vs), 943 (s), 842 (vs); ^{1}H NMR ($CDCl_3$) 7.31−7.14 (10H, m), 4.77 (1H, t, 6), 2.91 (2H, d, 6), −0.16 (9H, s); ^{13}C NMR ($CDCl_3$) 144.9, 139.1, 136.0, 129.8, 128.0, 127.0, 126.1, 125.8, 76.4, 47.5, −0.3.

4-Hydroxy-1-nonene (14) [35192-73-5]. This reaction was done on a 1.00 mmol scale, and the crude product was purified by flash column chromatography (hexanes/Et_2O gradient) to give 33 mg of the homoallylic alcohol as a clear, colorless oil (>99% pure by GC, 23% yield): IR (CCl_4) 3629 (b, m) 3592 (b, m), 3080 (m), 2957 (vs), 2862 (vs), 1642 (s), 1069 (s), 1024 (s), 995 (vs), 918 (vs); ^{1}H NMR ($CDCl_3$) 5.84 (1H, m), 5.15 (2H, m), 3.65 (1H, m), 2.32 (1H, m), 2.13 (1H, m), 1.59 (1H, d, 4), 1.34 (8H, m), 0.89 (3H, t, 6); ^{13}C NMR ($CDCl_3$) 134.9, 118.0, 70.7, 41.9, 36.7, 31.8, 25.3, 22.6, 14.0.

4-Hydroxy-5-phenyl-1-hexene (16) [77383-06-3]. This reaction was done on a 5.00 mmol scale, and the crude product was purified by flash column chromatography (hexanes/Et_2O gradient) to give 935 mg of the benzyl alcohol as a clear, colorless oil in 73% yield (97% pure by GC, 85:15 erythro:threo as determined by GC and ^{1}H NMR). Data given for erythro: IR (CCl_4) 3685 (b, w), 3589 (b, m), 3082 (m), 2978 (s), 1690 (vs), 1640 (m), 1265 (vs), 1012 (vs), 997 (vs), 992 (s); ^{1}H NMR ($CDCl_3$) 7.34−7.20 (5H, m), 5.80 (1H, m), 5.11 (2H, m), 3.71 (1H, dt, 5 and 4), 2.77 (1H, dt, 7 and 7), 2.18 (1H, m), 2.03 (1H, m), 1.72 (1H, bs), 1.34 (3H, d, 7); ^{13}C NMR ($CDCl_3$) 144.4, 135.0, 128.4, 127.7, 126.4, 118.0, 75.0, 45.3, 39.5, 16.3.

1-Allyl-1-(trimethylsiloxy)cyclohexane (20). This reaction was done on a 2.00 mmol scale, and the crude product was purified by flash column chromatography (hexanes/Et_2O gradient) to give 120 mg of the homoallylic trimethylsilyl ether as a clear, colorless oil (98% pure by GC, 28% yield): IR (CCl_4) 3076 (m), 2939 (vs), 1639 (m), 1249 (vs), 1065 (vs), 897 (m), 843 (m); ^{1}H NMR ($CDCl_3$) 5.86 (1H, m), 5.03 (2H, m), 2.26 (2H, d, 6), 1.62−1.26 (10H, m), 0.12 (9H, s); ^{13}C NMR ($CDCl_3$) 135.0, 116.8, 46.3, 38.0, 25.8, 22.5, 2.7.

1-Allyl-1-(trimethylsiloxy)cyclopentane (22). This reaction was done on a 2.00 mmol scale, and the crude product was purified by flash column chromatography (hexanes/Et_2O gradient) to give 38 mg of the homoallylic trimethylsilyl ether as a clear, colorless oil (89% pure by GC, 9% yield): IR (CCl_4) 3077 (m), 2961 (vs), 1639 (m), 1262 (vs), 1250 (vs), 1070 (vs), 1056 (vs), 861 (vs), 843 (vs); ^{1}H NMR ($CDCl_3$) 5.89 (1H, m), 5.04 (2H, m), 2.31 (2H, dt, 7 and 2), 1.78−1.50 (8H, m), 0.11 (9H, s).

Synthesis of 4-(*N*-Phenylamino)-4-phenyl-1-butene (24). Benzylideneaniline (905 mg, 5 mmol), allyltrimethylsilane (7.95 mL, 50 mmol), and TBAT (5.40 g, 10 mmol) were dissolved in THF (25 mL). The reaction mixture was heated at 70 °C and monitored by GC. After 30 h, the reaction had stopped at 89% completion. The THF and excess allyltrimethylsilane were evaporated at reduced pressure. The concentrate was then redissolved in 100 mL of 50/50 Et_2O/EtOAc, chilled to 5 °C for 2 h, and filtered to remove any excess TBAT. The filtrate was washed with water (2 × 50 mL) and brine (50 mL) and then concentrated to a red oil at reduced pressure. The red oil was purified by flash column chromatography (hexanes/CH_2Cl_2 gradient) to give 824 mg (95% pure

by GC, 79% yield) of a light yellow oil which darkens over time: IR (CCl_4) 3421 (b, m), 3058 (m), 2981 (m), 1639 (m), 1605 (vs), 1505 (vs), 1261 (m), 924 (s); ^{1}H NMR ($CDCl_3$) 7.44 (4H, m), 7.22 (1H, m), 7.06 (2H, m), 6.63 (1H, m), 6.49 (2H, m), 5.74 (1H, m), 5.17 (2H, m), 4.37 (1H, t, 5), 4.14 (1H, bs), 2.61 (1H, m), 2.51 (1H, m); ^{13}C NMR ($CDCl_3$) 147.3, 143.6, 134.7, 129.1, 128.6, 127.7, 127.0, 126.3, 117.4, 113.5, 57.1, 43.3.

Alkylation of TBAT-Generated Carbanions with Alkyl Halides. In each reaction, the corresponding trimethylsilyl reagent (5 equiv for entries 1−3 of Table 2 or 10 equiv for entries 4−7 of Table 2), the electrophile (1 equiv), and TBAT (2 equiv) were dissolved in THF (to give a 0.2 M solution of the electrophile) and heated at 70 °C or less. By doubling the amount of the allyltrimethylsilane reagent (from 5 to 10 equiv), the reaction time was generally cut in half. The reactions were followed by GC. The following example is illustrative of the protocol.

Synthesis of Pentadecene (36) [13360-61-7]. 1-Bromododecane (248 μL, 1.00 mmol), allyltrimethylsilane (1.59 mL, 10.0 mmol), and TBAT (1.08 g, 2.00 mmol) were dissolved in THF (5 mL). The clear, colorless solution was heated in a 70 °C oil bath for 24 h under N_2 and then the THF and excess allyltrimethylsilane were evaporated at reduced pressure. The concentrate was extracted with several portions (10 mL) of Et_2O until none of the desired product remained in the Et_2O insoluble phase as determined by GC. The Et_2O phase was then washed with water (2 × 50 mL) and brine (50 mL), dried ($MgSO_4$), and evaporated at reduced pressure. The crude oil was purified by flash column chromatography (hexanes) to give 182 mg of a clear and colorless oil (97% pure by GC, 87% yield): IR (CCl_4) 3077 (w), 2929 (vs), 1642 (m); ^{1}H NMR ($CDCl_3$) 5.82 (1H, m), 4.96 (2H, m), 2.04 (2H, m), 1.28 (22H, m), 0.88 (3H, t, 6); ^{13}C NMR ($CDCl_3$) 139.2, 114.1, 33.8, 31.9, 29.7 (b), 29.5, 29.4, 29.2, 29.0, 22.7, 14.1; LRMS 210.4 (9), 182.3 (4), 140.2 (6), 125.2 (13), 110.3 (32), 97.2 (73), 83.1 (89), 70.1 (82), 56.6 (95), 54.4 (100).

1-Phenyl-1-tetradecyne (30). This reaction was done on a 5.00 mmol scale, and the crude product was purified by flash column chromatography (hexanes) to give 1.10 g of the phenylalkyne as a clear, colorless oil (>99% pure by GC, 81% yield): IR (CCl_4) 3085 (w), 2928 (vs), 2857 (vs), 2236 (w), 1943 (w), 1875 (w), 1800 (w), 1600 (w); ^{1}H NMR ($CDCl_3$) 7.38 (2H, m), 7.24 (3H, m), 2.38 (2H, t, 7), 1.59 (2H, m), 1.43 (2H, m), 1.25 (16H, m), 0.88 (3H, t, 7); ^{13}C NMR ($CDCl_3$) 131.5, 128.1, 127.4, 124.1, 90.4, 80.5, 31.9, 29.7, 29.6, 29.5, 29.3, 29.2, 28.9, 28.8, 22.7, 19.4, 14.1.

1-(2-(1,3-Dithianyl))dodecane (31). This reaction was done on a 3.76 mmol scale, and the crude product was purified by flash column chromatography (hexanes/Et_2O gradient) to give 586 mg of the dithiane as a clear, colorless oil (95% pure by GC, 52% yield): IR (CCl_4) 2929 (vs), 2856 (vs), 1424 (m); ^{1}H NMR ($CDCl_3$) 4.04 (1H, t, 7), 2.83 (4H, m), 2.60 (1H, t, 7), 2.59 (1H, t, 7), 1.74 (2H, m), 1.25 (20H, m), 0.88 (3H, t, 7); ^{13}C NMR ($CDCl_3$) 47.6, 35.4, 31.9, 31.0, 30.4, 29.6, 29.5, 29.4, 29.3, 29.2, 28.9, 26.6, 26.0, 22.6, 14.0.

1-Phenyltridecane (32) [123-02-4]. This reaction was done on a 3.10 mmol scale, and the crude product was purified by flash column chromatography (hexanes) to give 693 mg of the alkane as a clear, colorless oil (98% pure by GC, 84% yield): IR (CCl_4) 3085 (w), 2928 (vs), 2857 (vs), 1940 (w), 1868 (w), 1800 (w), 1604 (m); ^{1}H NMR ($CDCl_3$) 7.26 (2H, m), 7.16 (3H, m), 2.59 (2H, t, 8), 1.60 (2H, m), 1.25 (20H, m), 0.88 (3H, t, 7); ^{13}C NMR ($CDCl_3$) 143.0, 128.4, 128.2, 125.5, 36.0, 31.9, 31.5, 29.7, 29.6, 29.5, 29.4, 22.7, 14.1.

4-Phenyl-1-butene (38) [768-56-9]. This reaction was done on a 5.00 mmol scale, and the crude product was purified by flash column chromatography (pentane) to give 409 mg of the alkene as a clear, colorless oil (>99% pure by GC, 62% yield). Although the reaction went to completion to give a single product, some product was lost during workup and purification due to its volatility: IR (CCl_4) 3084 (m), 2983 (m), 1939 (w), 1860 (w), 1830 (w), 1803 (w), 1641 (m), 913 (s), 821 (vs); ^{1}H NMR ($CDCl_3$) 7.20 (5H, m), 5.85 (1H, m), 5.01 (2H, m), 2.71 (2H, t, 7), 2.37 (2H, m); ^{13}C NMR ($CDCl_3$) 141.8, 138.1, 128.4, 128.3, 125.8, 114.7, 35.5, 35.4.

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Supporting Information Available: ^{1}H and ^{13}C NMR spectra of compounds **6**, **20**, **22**, **24**, **30**, and **31** (16 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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