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FLUORIDE CATALYZED REACTION OF SILYLACETYLENES WITH CARBONYL COMPOUNDS

I. KUWAJIMA,* E. NAKAMURA and K. HASHIMOTO

Department of Chemistry, Tokyo Institute of Technology, Meguro, Tokyo 152, Japan

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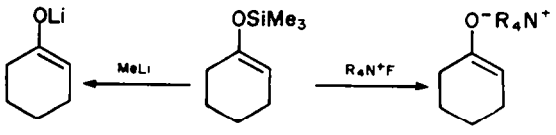
Abstract—(Phenylethynyl)trimethylsilane undergoes nucleophilic addition to a variety of carbonyl compounds in the presence of a catalytic amount of fluoride anion to give silylated propargyl alcohol derivatives. The reaction fails with enolizable enones and cyclopentanone. The reaction of bis(trimethylsilyl)acetylene does not stop at the stage of monoadduct, and affords a considerable amount of symmetric bisadduct. (Trimethylsilyl)acetylene attacks 4-t-butylcyclohexanone from the axial side, as other metal acetylides do. Although much slower than the above cases, the reaction of alkynyltrimethylsilanes also proved successful. The reactivities of these (trimethylsilyl)-acetylenes are discussed in terms of the reaction mechanism and the nature of the reactive species, and also compared with those of the silylated enols under similar conditions.

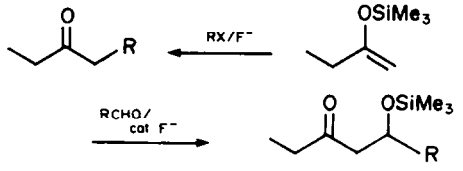
Of the three general categories of reactive intermediates in organic chemistry, i.e. carbanion, carbocation, and radical, the chemistry of carbanion may claim to be the most powerful and reliable for achieving C–C bond forming synthetic sequences. Removal of acidic protons and reductive cleavage of C–halogen bond, e.g. Grignard reaction, have been the standard entries to the carbanion chemistry.[1] The rapid development in this field after the 1960's, brought about by the availability of various alkyllithiums, has been dramatic, and its influence far-reaching. In addition, innovations in carbanion chemistry have been made by introduction of the concepts of organometallic chemistry.[2] A recent trend in synthetic organic chemistry is clearly centered around the development of milder and more selective processes. This has grown out of the demands produced by the ever increasing complexity of the molecules which challenge synthetic chemists. The fusion of carbanion and organometallic chemistry[3] in the past decade is in part ascribed to such demands. It is in this context that we studied the fluoride-mediated activation of organosilicon compounds in the past several years.

Temporary storage of the regio- ans stereochemical integrity of an enolate anion in the form of an enol silyl ether (1)[4] is an early example of the deliberate use of silicon atoms for organic synthesis.[5] The transformation of the enol silyl ether to the corresponding enolate anion, in Stork's original report[4] was achieved with the aid of methyllithium, and inherently confined to the generation of Li enolates. Our interest in discovering a milder method for enolate generation as well as the possibility of preparing a naked enolate anion 2 (an anion not complexed with the counteraction) led us to examine the action of tetraalkylammonium fluorides. We initiated this work because we suspected that the complete absence of covalent interaction between the enolate moiety and the cation portion should affect the reactivity of 2.



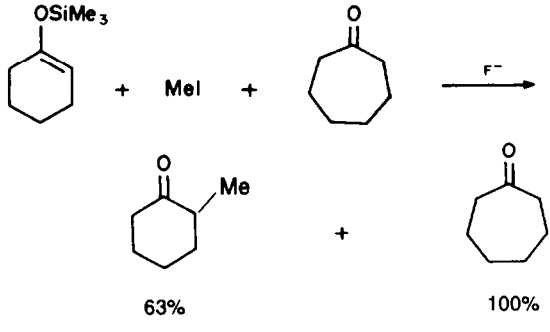
1 2

At the time we initiated the studies,[6] only a few synthetic reactions which made use of the high affinity of silicon and fluorine atoms were known. The ability of the fluoride anion to aid the protonolysis of Si–Oxygen bonds was receiving attention for the purpose of removing silyl protective groups.[7] Generation of nucleophilic species by the action of the fluoride anion on (perhalogenophenyl)-trimethylsilane had been reported,[8] but the real potential of fluoride anion in organic synthesis was first demonstrated by the alkylation reaction of enol silyl ethers.[1] Treatment of a mixture of an enol silyl ether and an alkyl halide with a stoichiometric amount of a tetraalkylammonium fluoride afforded the regiospecifically alkylated product in good yield. The reaction was then extended to the fluoride-*catalyzed* aldol reaction (eqn 1).[9]



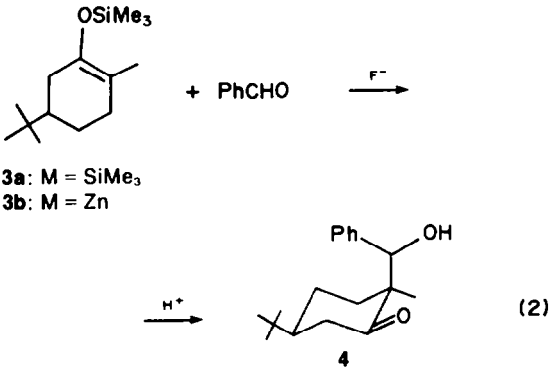
(1)

During these studies were found several notable deviations of the behaviour of naked enolates[10] from that of the standard metal enolates were found. For instance, the reaction proved to have broad tolerance of compatible functionalities:[6,9] the alkylation reaction could be carried out in the presence of molecules of another ketone without appreciable complication.[6b]



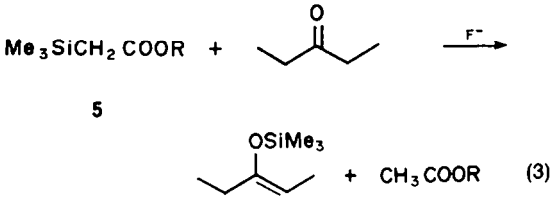
The aldol reaction showed a remarkable stereoselec-

tivity. The reaction of the enol silyl ether **3a** gave exclusive axial adduct **4**, while the corresponding zinc enolate **3b** showed only *ca* 60% axial selectivity (eqn 2).[9]



(2)

The fluoride-mediated method also made accessible the enolate anions of esters.[11] A dramatic effect of the cation was observed. As is well known, the commonly encountered ester enolates such as Zn or Li enolates react cleanly with ketones to give β-hydroxyesters.[12] The naked enolate of alkyl acetates generated from 2-trimethylsilylacetates **5** however, did not give *any* trace of adducts; instead, it deprotonated the substrates. The overall result was the transfer of the silyl group from **5** to the ketone;[11b,13] interestingly, a notable stereoselectivity of the double bond geometry was observed[11c].



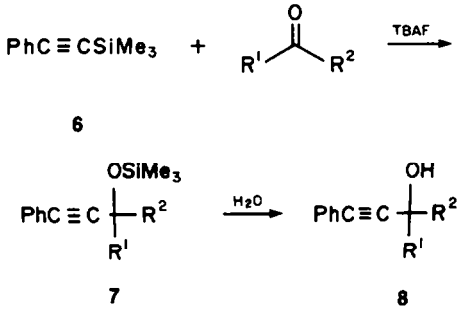
(3)

Extending the research to other carbon nucleophiles, we turned to the chemistry of acetylenes,[14] which is described here in detail. Following our initial studies, the fluoride-mediated activation method,[5] as represented by the intramolecular applications,[15] has been widely used, taking advantage of the mild reactivity of the fluoride anion.

RESULTS AND DISCUSSION

The reactivities of silylacetylanes were examined chiefly by using (phenylethynyl)trimethysilane(**6**), the Si–C bond of which was cleaved most easily by a fluoride anion (eqn 4). On the basis of the observations made in related reactions,[9,11] tetrabutylammonium fluoride hydrate (BTAF) was used in tetrahydrofuran (THF) to get satisfactory results. Dimethoxyethane (DME) was also a suitable solvent. Benzyltrimethylammonium fluoride[6] was less efficient and offered no advantage over TBAF. Potassium ethoxide complexed with 18-crown-6 (KOEt/18-crown-6) was even less efficacious.

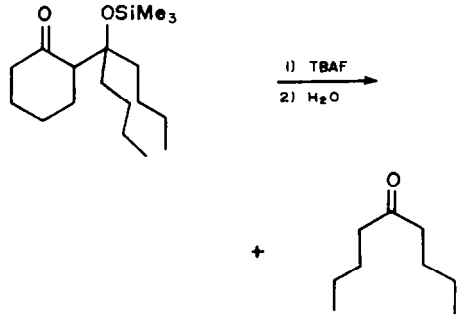
In the presence of about 5 mol% TBAF, the silylacetylene **6** smoothly reacted at −20° with a variety of carbonyl compounds. The reaction mixture was routinely warmed up to 0° or to room temperature. The reaction was kinetically controlled, and the results did not seem to be affected by such procedure (*vide infra*). Aqueous workup without precaution tended to give a mixture of the silylether **7** and the hydroxyl compound **8**, but dilution of the mixture with hexane prior to the usual workup allowed the isolation of **7** in good yield. Removal of the silyl group from **7** could be effected by treating the adduct with aqueous acetic acid or potassium fluoride in methanol either before or after the workup.



(4)

The reaction of **6** with carbonyl compounds of various structural types was examined (Table 1). Aliphatic aldehydes gave the expected adducts consistantly in high yields (entries 2, 3). Aromatic aldehydes gave somewhat lower yields (entry 1). A peculiar reactivity spectrum was observed in the reaction with ketones. Aliphatic ketones (entries 4, 5) proved to be good substrates for this reaction with one exception: the reaction of cyclopentanone (entry 9) indicated little incorporation of the phenylacetylene moiety in the product mixture, and afforded ketonic self-condensation products. Among conjugated ketones, non-enolizable benzophenone and benzalacetophenone (entries 7, 8) gave satisfactory results. Other common conjugated ketones, however, did not give appreciable amounts of adducts (entries 10–14). A rather interesting contrast was found between two seemingly equivalent phenones. Propiophenone reacted smoothly, whereas acetophenone virtually failed to react (entries 6, 10).

The fluoride-catalyzed aldol reaction of enol silyl ethers (eqn 1) also showed reluctance to give adducts with ketones. This has been shown to be due to an unfavorable thermodynamic factor (eqn 5) as well as a kinetic one.[9b]



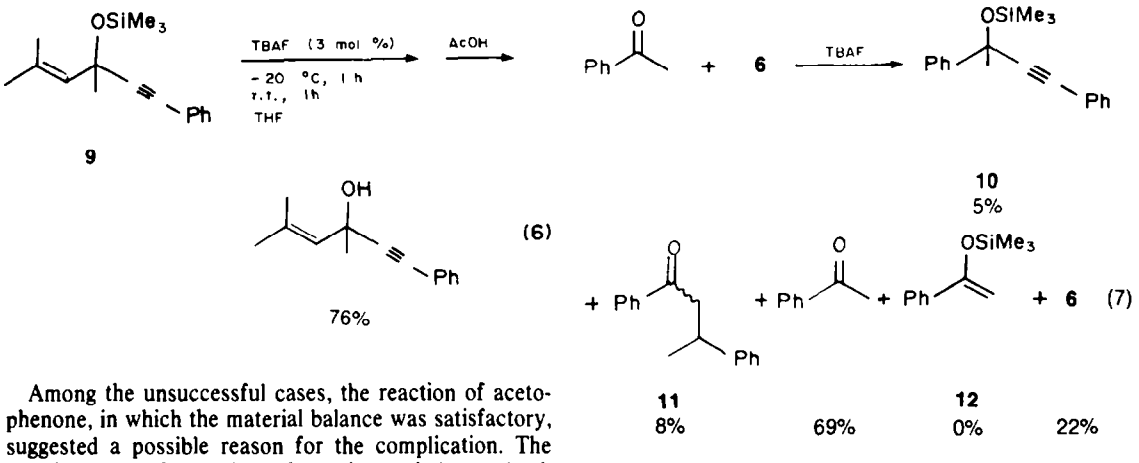
(5)

The thermodynamic stability of the enone adduct was therefore examined. The adduct **9** prepared via the lithium acetylide was subjected to the usual reaction conditions. The compound was stable, and recovered unchanged (eqn 6). Kinetic argument does not seem to solve the problem either, since highly conjugated, thus less reactive, ketones did, in fact, react smoothly (entries 7, 8). We did not observe evidence for the existence of a single-electron transfer process in these cases.

Table 1. The reaction of (phenylethynyl)trimethylsilane **6** with carbonyl compounds[a]

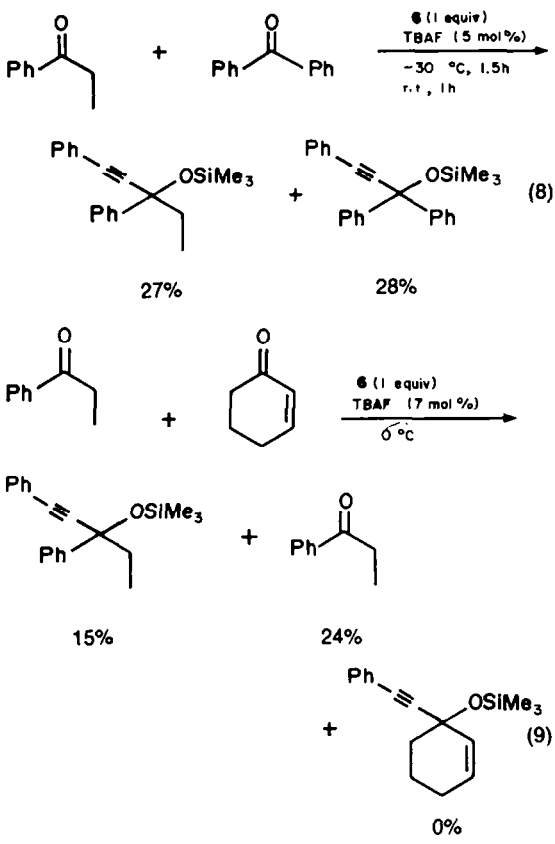
entry	carbonyl compounds	% yield
1	benzaldehyde	76
2	octanal	70
3	isoburaldehyde	(84)
4	5-nonanone	67
5	cyclohexanone	87
6	propiophenone	(84)
7	benzophenone	79
8	benzalacetophenone	83
9	cyclopentanone	0[b]
10	acetophenone	5[c]
11	2-cyclohexen-1-one	0
12	mesityl oxide	0[d]
13	β-ionone	12[e]
14	benzalacetone	10

[a] The reactions were carried out at -20 °C (ca. 30 min), and then at 0 °C or room temperature (1 h), using an almost equimolar amount of 6, and ca. 5 mol % of TBAF in THF. [b] 2-Cyclopentylidenecyclopentanone (ca. 40 %) was obtained. [c] See the text. [d] The ketone (100%) and 6 (67%) were recovered (GLC analysis). [e] The ketone was recovered (47%).

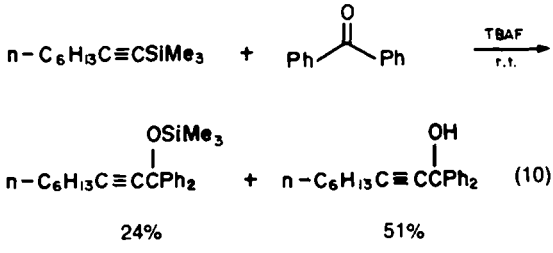


Among the unsuccessful cases, the reaction of acetophenone, in which the material balance was satisfactory, suggested a possible reason for the complication. The reaction, even after prolonged reaction period, gave back the starting ketone, together with small amounts of the adduct **10** and the enone **11** (eqn 7). The formation of enol silyl ether **12**, expected in analogy to the reaction of alkyl trimethylsilylacetates[11] (*cf* eqn 3), was not observed, and thus does not account for the recovery of the ketone. Considering also the case of cyclopentanone (entry 9). We ascribed the anomalies to the formation of enolate anion. Moreover, the addition reaction appeared to be inhibited by the side reaction, which in fact was borne out by the competition experiments.

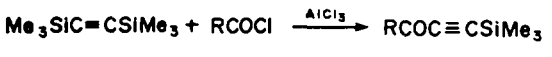
Competition between "good" substrates were carried out first. Treatment of an equimolar mixture of **6**, propiophenone, and benzophenone with TBAF afforded virtually equal amounts of the respective adducts in good combined yield (eqn 8). In a similar experiment using propiophenone, and cyclohexenone, the propiophenone adduct was obtained in a greatly diminished yield, and yet none of the cyclohexenone adduct was detected (eqn 9).



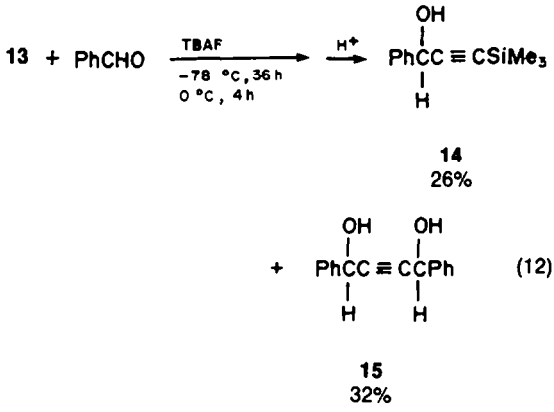
We then turned our attention to other acetylene derivatives to examine the scope of the reaction. The reaction of octynyltrimethylsilane in the presence of a catalytic amount of TBAF was invariably slower than those of **6** irrespective of the carbonyl partner. Typically, the reaction with benzophenone gave a mixture of the expected adducts in 75% combined yield after 18 hr in the presence of about 10 mol% of the catalyst (eqn 10). It is reasonable to assume that the inductive effect of the aliphatic chain slowed down the rate of Si–C bond cleavage.



The reaction of bis(trimethylsilyl)acetylene[16] (**13**) was investigated next. It was of interest to see if we could activate the two silyl groups sequentially with the aid of fluoride anion. Utilization of one of these two silyl groups for carbon–carbon bond formation has been achieved under Lewis-acid catalysis,[17] and provided a useful method for acylating acetylenes (eqn 11).

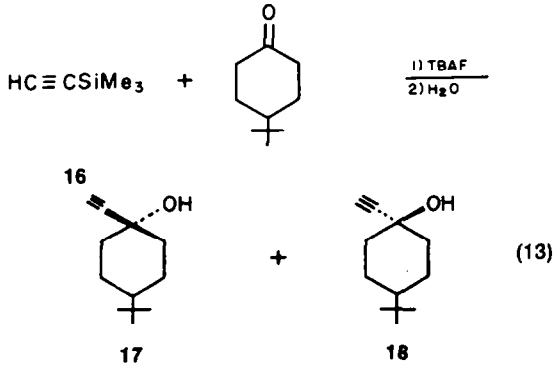


The TBAF-catalyzed reaction of **13** (1 equiv) and benzaldehyde, however, gave a mixture of **14** and **15** of which the latter slightly predominated (eqn 12). It appeared that the reactivity of the monoadduct **14** is higher than that of the starting acetylene **13**. A recent report[18] using potassium fluoride/18-crown-6 claims a much higher yield of the monoadduct without referring to the formation of the diadduct. The reason for the observed difference is not apparent at the moment.

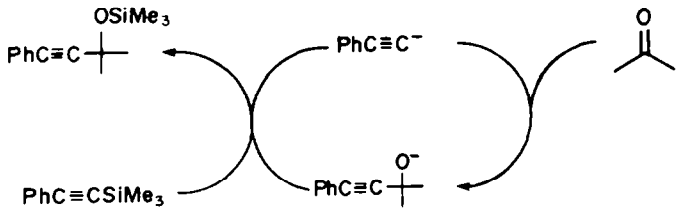


The reaction of trimethylsilylacetylene (**16**), readily available on a large scale,[19] was the subject of the subsequent investigation. Especially intriguing was the possibility of using the stereochemical outcome as a mechanistic probe, since we know more about the chemistry of acetylene itself than that of the higher homologues.[20]

When a mixture of 4-t-butylcyclohexanone was treated with TBAF at room temperature, complete disapperance of the ketone was observed within 30 min. The crude adduct was treated with potassium fluoride in methanol to afford a mixture of **17** and **18** in 88% combined yield (eqn 13). Comparison of the ^{13}C NMR of this mixture with that of the authentic mixture[21] revealed the ratio of >90:10. The ratio of axial and equatorial attack was much the same as with sodium acetylide,[21] indicating that the reactive species in the present reaction behaves just like usual metal acetylides.



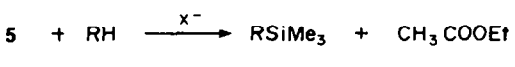
Reaction mechanism. On considering the mechanism of the present reaction, two different, yet related questions should be solved. One is concerned with the precise role of the fluoride anion, and the other with the nature of the reactive species. We took the results of ethoxide catalysis (*vide supra*) as an important clue for elucidating these points, and examined the details.



Scheme 1.

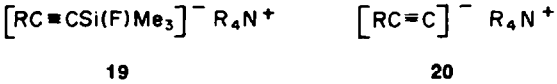
Though much slower and less clean than the TBAF catalysis, the coupling of **6** and cyclohexanone was achieved in the presence of KOEt/18-crown-6 (5 mol% catalyst, THF, 0°, 3 hr; 45% yield). As brief consideration would reveal it, this result points to the operaton of an autocatalytic mechanism[11d] (Scheme 1).

On the other hand, the reaction of benzaldehyde under similar conditions did not give any of the expected adduct, although the aldehyde readily disappeared at 0°. In view of the presence of vinylic protons (^{1}H NMR) and conjugated ketonic CO groups (IR) in the isolated products, the complication was not due to the base catalyzed degradation of the starting materials, but to that of the adducts initially formed. The formation of side products was minimal under the TBAF catalysis. A large difference in the reaction rate between the TBAF catalysis and the ethoxide catalysis stands in contrast with the high catalytic ability of an alkoxide/crown ether complex (just as good as TBAF) in the catalyzed reaction of alkyl trimethylsilylacetate **5**[11d] (eqn 14). Taking the product and the rate analysis into account, we conclude that fluoride anion, being a unique and efficient catalyst, plays a key role in the present reaction.[9b]



RH = ketones, alcohols, thiols (14)
X⁻ = R⁻, CN⁻, MeO⁻

Our next concern was focused on the nature of the reactive species. Two possibilities were readily conceived: a fluoride-complexed siliconate **19** and a naked acetylide anion **20**. The formation of the naked anion has



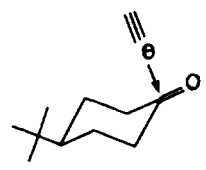
19 **20**

been shown to occur by the attack of the fluoride anion on trimethylsilyl enol ethers[10] and 2-trimethylsilylacetates (**5**),[11d] possessing highly polarizable Si–O or Si–C bonds. On the other extreme, the less polarizable Si–C bond of (perhalogenophenyl)trimethylsilane has been postulated to form a siliconate complex.[8]

The fluoride-mediated carbanion formation has recently had considerable success in gas phase chemistry[22] (eqn 15). A variety of anions ranging from acetylide to allyl and phenyl anions were generated and characterized by the action of a fluoride anion on the respective Si-containing precursors. The reaction stopped at the stage of the ate complex when the leaving anion R^- was poorly stabilized, e.g. R = Me. Interestingly, the Si–O bond (R = OMe) did not cleave in gas phase, where, the resultant oxygen anion cannot be stabilized by solvation, as it can in solution.

(15)

With this background, we felt that examination of the stereochemistry of the reaction with an appropriate substrate would be useful for elucidating the nature of the reactive species, since the siliconate **19**, if it were a discrete *reactive* intermediate, should have a much bigger steric damand than the naked anion **20**. It is established[20] that any nucleophile bigger in size than simple hydride and acetylide tends to attack 4-t-butylcyclohexanone from the equatorial side. An acetylide anion, being linear in shape, is considered to attack the ketone bia a transition state like **21**. The high axial selectivity of the acetylide generated from **16** (eqn 13) is certainly in line with such a transition state. If the present reaction were to proceed via **19**, any type of the (early) transition states, e.g. **22** being more sterically congested than **21**, would have enhanced the amount of equatorial approach of the reagent.[23]



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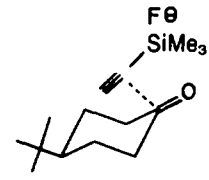

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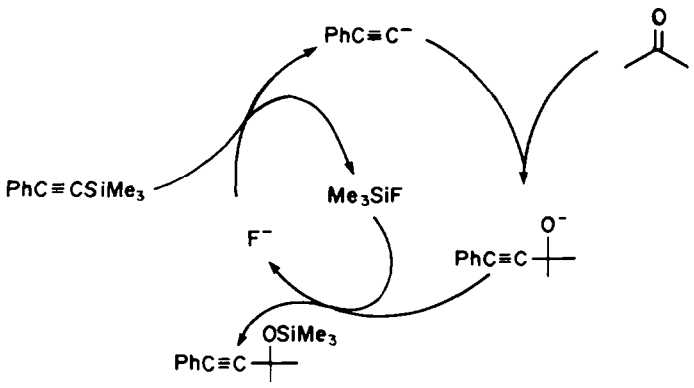
The mechanistic rationale thus deduced in depicted in Scheme 2. Rather puzzling results with enolizable enones may be reconciled with this scheme, if we assume that the enolate anion, less reactive than simple alkoxides, cannot be readily silylated by fluorotrimethylsilane. This assumption does not seem unreasonable, and is compatible with the mechanism of the related aldol[9b] and silylation reaction (eqn 3).[11d]

As pointed out at the outset, the reactivities of anions depend on the nature of the countercations. It is certainly true with the acetylide anion discussed here. Magnesium and lithium acetylides are highly reactive nucleophiles and they add indiscriminately to aldehydes and ketones, whereas the character of the naked acetylide is much less of a nucleophile and more of a base. Such a trend is also observed in the fluoride-catalyzed reactions of enol silyl ethers (**1**) and silylacetates (**5**). It is therefore intriguing to compare, at this point, the substrate-dependent reactivity spectrum of the naked anions of acetylide, ester enolates,[11] and ketone enolates.[9]

In Table 2 are listed the results of the TBAF-catalized reaction of the three organosilicon compounds, **1**, **5** and **6**. The acetylide **6** is the most nucleophilic of all, and gives adducts in good yield with some exceptions, e.g.



Scheme 2.

Table 2. Flouride-catalyzed reactions of organosilicon compounds with carbonyl compounds[a]

	PhCHO	⌒CHO	RCH_2CHO	O H	⌒O H	PhCOPh	RCOOR'
1	+	+	+	-	-	-	-
5	+	+	-[b]	- (silyl transfer)	-	+	-
5	+	+	+	+	-	+	-

[a]Signs refer to the following: +, adduct formation; -, recovery of the starting carbonyl compounds except some cases. [b]The major reaction path was the polycondensation of the aldehydes.

enolizable enones (*vide supra*). The silylacetate **5** is also quite reactive, as evidenced by adduct formation with benzophenone. Such high nucleophilicity of **5**, however, is greatly modified by the occurrence of the silyl transfer reaction, the consequence of initial proton abstraction from the substrates (eqn 3). The lack of adduct formation even with aliphatic (enolizable) aldehydes is due to such deprotonation reactions (and the polymerization which follows).

Enol silyl ethers (**1**) are the least reactive of the three. Aldehydes form adducts in good yield, but ketones fail completely. We did not detect the occurrence of the silyl transfer reaction. These three classes of compounds invariably failed to give addition products with enolizable enones; the reasons, however, are different for all. The acetylide **6** caused enolization of the substrate, which deactivated the catalytic cycle (*vide supra*). The ester **5** also enolized the ketone, but this was followed by the silyl transfer reaction (eqn 3). The case of enol silyl ethers (**1**) is a thermodynamically disfavoured process (eqn 5). The general absence of the silyl transfer reaction with **1** and **6** is interesting in view of the facile transfer from **5** to various ketones. The difference parallels the mechanistic change (real fluoride-catalysis *vs* autocatalysis *cf* Scheme 1 and 2), and rests on the ease of the release of the silyl group from the respective Si starting materials; namely, the silylacetate (**5**) more readily transfers its silyl group than fluorotrimethylsilane, whereas **1** and **6** do so less readily.

EXPERIMENTAL

General data are described previously.[6b] ^{13}C NMR were taken on a JEOL XL-100 spectrometer and were recorded in ppm down field from internal TMS.

3-Trimethylsiloxy-1,3-diphenyl-1-propyne. A soln of (phenylethynyl)trimethylsilane (287 mg, 1.65 mmol) and benzaldehyde (159 mg, 1.50 mmol) was treated with 13 mg TBAF (0.05 mmol) at −20° for 5 min and then at 0° for 1 hr. The red mixture was diluted with hexane, and filtered. After concentration, the crude oil was distilled to afford 318 mg of the title compounds (75.7%): b.o. 105–110° (bath temp), 0.04 mm. IR (neat) 1600 (w), 1060 (s, C–O), 840 (s, TMS); NMR (CCl_4) 0.02 (s, TMS), 5.70 (S, –CH–O), 7.10–7.60 (m, aromatic protons); mass spectrum *m/e* (rel %) 280 (M^+, 17), 2.65 ($M^+ - 15$, 7), 191 (38), 179 (46), 147 (80), 105 (100), 77 (73), 75 (46), 73 (91): high resolution mass spectrum 280.1278 (Calc. for $C_{18}H_{20}OSi$: 280.1282).

3-Trimethylsiloxy-1-phenyl-1-decyne. A mixture of (phenylethynyl)trimethylsilane (400 mg, 2.30 mmol) and octanal (256 mg, 2.00 mmol) in 2.5 ml THF was treated at 0° with TBAF (16 mg, 0.06 mmol) for 1.5 hr. The mixture was diluted with hexane, and filtered through Celite to afford 520 mg of the crude product, which was homogeneous on TLC. Purification on preparative TLC gave 424 mg of the title compound (70%), which was identical with an authentic sample: b.p. 140–142°, 1.5 mm: IR (neat) 1600 (w), 1087 (s), 840 (s),; NMR (CCl_4) 0.19 (s, 9H, CH_3Si), 0.62–2.05 (m, 15H, CH_3, CH_3), 4.51 (t, J = 6 Hz, 1H, CHO), 7.10–7.60 (m, 5H, C_6H_5): mass spectrum *m/e* (rel %) 302 (M^+, 1), 287 ($M^+ - 15$, 2), 231 (9), 203 (100), 159 (17), 147 (51), 131 (44), 129 (30), 75 (37), 73 (85); high resolution mass spectrum 302.2068 (Calc. for $C_{19}H_{30}OSi$: 302.2065).

4-Methyl-1-phenyl-1-pentyn-3-ol. A soln of (phenylethynyl)trimethylsilane (435 mg, 2.50 mmol) and isobutyralde-

hyde (194 mg, 2.70 mmol) in 2 ml THF was treated with 23 mg TBAF (0.09 mmol) at −20° for 1 hr. The yellow mixture was then treated with 1.5 ml AcOH/H_2O (1:2), and allowed to warm to room temp. After 5 hr, the colorless soln was diluted with 5 ml ether, and neutralized with $NaHCO_3$ aq. The organic layer was separated and the aqueous layer was extracted twice with ether (5 ml × 2). The combined extract was dried, and concentrated. The residual oil was purified by bulb-to-bulb distillation to give 364 mg (83.6%) as a colorless oil: bp 85° (bath temp. 0.09 mm); IR (neat) 3350 (br, OH), 1030 (s, C–O); NMR (CCl_4) 1.03 and 1.06 (two d, J = 7H_2, 6H, CH_3–), 1.6–2.3 (m, 1H, CH–CH_3), 3.00 (s, 1H, OH). 4.37 (d, J = 5.5H_2, 1H, CH–O], 7.1–7.6 (m, 5H, aromatic protons). (Found: C, 82.82; H, 8.24. Calc. for $C_{12}H_{14}O$: C, 82.72; H, 8.10).

5-(*Phenylethynyl*)-5-*trimethylsiloxynonane*. A soln of (phenylethynyl)trimethylsilane (447 mg, 2.60 mmol) and dibutyl ketone (3555 mg, 2.50 mmol) in 3 ml THF was added to TBAF (23 mg, 0.09 mmol) kept at 0°. The colorless mixture was stirred for 1.5 hr at 0°. No ketone was detected on TLC, and the mixture was concentrated *in vacuo*. Bulb to bulb distillation of the crude product afforded the title compound (522 mg, 67%); b.p. 90°, 0.04 mm; IR (neat) 1040 (br, C–O), 840 (s, TMS); NMR (CCl_4) 0.32 (s, TMS, 9H) 0.95–2.55 (m, 18H, CH_3–, –CH_2–) 7.25–7.6 (m, 5H, aromatic protons). Mass spectrum, 10 ev (relative %); 301 (3, M^+–15), 259 (100, M^+–57), 85 (21), 75 (5), 73 (5), 57 (9).

1-*Trimethylsiloxy*-1-(*phenylethynyl*)*cyclohexane*. A soln of (phenylethnyl)trimethylsilane (287 mg, 1.65 mmol) and cyclohexanone (147 mg, 1.50 mmol) in 2 ml THF was treated with 14 mg TBAF (0.05 mmol) at −20° for 30 min, and then at 0° for 1 hr. The yellow mixture was diluted with hexane, and filtered. After concentration, the crude yellow oil, which was chromatographically pure, was purified on preparative TLC to afford 354 mg of the title silyl ether (86.8%): b.p. 115–117°, 1.0 mm; IR (neat) 835 (s, TMS); NMR (CCl_4) 0.20 (s, TMS), 1.05–2.60 (m, 10H, –CH_2–), 7.10–7.55 (m, aromatic protons); mass spectrum *m/e* (rel%) 272 (M^+, 20), 257 (M^+ − 15, 23), 242 (12), 228 (100), 159 (14), 155 (12), 141 (6), 129 (9), 115 (14), 75 (38), 73 (58), 55 (20): high resolution mass spectrum 272.1576 (Calc. for $C_{17}H_{24}O$ Si; 272.1595).

3-*Hydroxy*-1,3-*diphenyl*-1-*pentyne*. A mixture of propiophenone (134 mg, 1.00 mmol) and (phenylethynyl)-trimethylsilane (201 mg, 1.20 mmol) in 2 ml DME was treated at −40° with TBAF (26 mg, 0.01 mmol), and the mixture was stirred at 20° for 30 min. The mixture was treated with dil ethanolic HCl, diluted with water and ether. The organic layer was separated, washed with NaCl aq, dried and concentrated. The crude oil was composed of a single product, and purified on preparative TLC to give 198 mg (84%) of the title compound; IR (neat) 3480 (br), 760 (vs), 701 (s), 691 (s). Silylation with Me_3SiCl/Et_3N gave the silylated material: IR (neat) 1250 (s), 1055 (s), 840 (S), 755 (s), 688 (s); NMR (CCl_4) 0.14 (s, 9H), 0.96 (t, J = 7.5 Hz, 3H), 1.97 (t, J = 7.5 Hz, 2H), 7.2–7.8 (m, 10H). (Found: C, 77.76; H, 7.90. Calc. for $C_{20}H_{24}O$ Si; C, 77.87, H, 7.84).

3-*Trimethylsiloxy*-1,3,5-*triphenyl*-4-*pentyn*-(E)-1-*ene*. A soln of (phenylethynyl)trimethylsilane (192 mg, 1.10 mmol) and benzalacetophenone (208 mg, 1.00 mmol) in 2 ml THF was treated with 9 mg TBAF (0.034 mmol) at −20° for 30 min and then at 0° for 30 min. The mixture was freed of the solvent and purified on preparative TLC (hexane) to afford 269 mg (70.3%): b.p. 160–165° (bath temp), 0.01 mm; IR (neat)2220 (vw), 1055 (s), 840 (s); NMR (CCl_4) 0.23 (s, 9H, $SiCH_3$), 6.30 (d, J = 8Hz, 1H, C–CH=), 6.91 (d, J = 8 Hz, 1H, Ar–CH=), 7.1–7.8 (m, 15H, aromatic protons); mass spectrum (70 eV) *m/e* (rel%) 382 (M^+, 8), 305 (2), 215 (4), 75 (100), 73 (15).

3-*Trimethylsiloxy*-1,3,3-*triphenyl*-1-*propyne*. To a soln of TBAF (35 mg, 0.13 mmol) in 2 ml THF at −20° was added a mixture of benzophenone (374 mg, 2.05 mmol) and (phenylethynyl)trimethylsilane (340 mg, 1.95 mmol) in 2 ml THF. The mixture was warmed up to 0° during 1 hr. A colorless oil obtained after concentration *in vacuo* was purified on preparative TLC (hexane). The fastest moving fraction contained the title compound (551 mg, 79%), and the second the starting ketone (50 mg). The third fraction was the free OH-form of the adduct (10 mg, 2%). The title compound showed the following spectra: IR (neat) 2200 (w), 1245 (s), 1055 (s), 870 (s), 835 (s), 750 (s), 690 (s): NMR (CCl_4) 0.25 (s, 9H), 7.3–7.7 (m, 15H). (Found: C, 80.65; H, 6.76. Calc. for $C_{24}H_{24}O$ Si: C, 80.85; H, 6.78).

Reaction of 1-*trimethylsilyl*-1-*octyne with benzophenone*. To a soln of TBAF (13 mg, 0.05 mmol) and benzophenone (182 mg, 1.00 mmol) in 1 ml THF was added a soln of 1-trimethylsilyl-1-octyne (200 mg, 1.10 mmol) in 1 ml of THF at 0°. The cooling bath was removed, and the mixture was stirred for 18 hr, with *ca* 20 mg TBAF added after 3 hr. The yellow mixture was freed of the bulk of the solvent on an evaporator, and the remaining oil was applied to preparative TLC. Three compounds were separated after purification twice on preparative TLC. They were designated as A, B and C according to the magnitude of R_f value.

A was 1-trimethylsiloxy-1,1-diphenyl-2-nonyne (86 mg, 23.6%): IR (neat) 1063 (s), 882 (s), 842 (s); NMR (CCl_4) 0.08 (s, 9H, $SiCh_3$), 0.7–1.8 (m, 9H, CH_3–, –CH_2–), 2.31 (unresolved t, J = 7 Hz, 2H, CH_2–C≡C, 7.1–7.65 (m, 10H, aromatic protons).

B was benzophenone (24 mg, 13.2% recovery).

C was 1-hydroxy-1,1-diphenyl-2-nonyne (149 mg, 50.9%): b.p. 130–140° (bath temp), 0.027 mm; IR (neat) 3500 (shoulder), 3420 (br), 1000 (m); NMR (CCl_4) 0.7–1.8 (m, 9H, CH_3–, –CH_2–), 2.30 (m, 3H, –CH_2C≡C), OH, this signal became unresolved t, J = 7 Hz, 2H, on D_2O treatment), 7.1–7.65 (m, 10H, aromatic protons). (Found: C, 86.02; H, 8.28. Calc. for $C_{21}H_{24}O$: C, 86.26; H, 8.27).

The reaction of (*trimethylsilyl*)*acetylene and* 4-*t-butylcyclohexanone*. To a mixture of the title ketone (154 mg, 1.00 mmol) and TBAF (26 mg) in 1.5 ml THF at −30° was added **16** (196 mg) via a microsyringe during 30 sec. The cooling bath was removed after 5 min, and the mixture was stirred at 18° for 1.5 hr. TLC analysis indicated the complete disappearance of the starting ketone. KF (0.3 g) in 1 ml MeOH was added, and the mixture was stirred for 3 days at room temp. Concentration and the usual aqueous workup afforded 158 mg of the adduct as white powder (88% yield) after removing the impurities via a silica gel column. This material was identical with the authentic mixture of **17** and **18** (89:11), made by the addition of ethynylmagnesium bromide to the ketone, by IR, ^1H NMR, and by TLC. The isomeric ration of **17** and **18** was determined as 93:7 by ^{13}C NMR comparison: ^{13}C NMR ($CDCl_3$) 21.76 (t, **18**), 24.75 (t, **17**), 27.61 (q), 32.24 (s), 39.26 (t, **18**), 40.25 (t, **17**), 47.04 (d), 69.45 (s), 72.78 (d), 87.17 (s).

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