highly reactive with the solvent CCl_4 and is not responsible for the formation of the phenoxymethyl-type radical. Furthermore, from the product analysis, it was found that two relevant products, 4-$ClCH_2OC_6H_4Cl$ and 4-$CH_3OC_6H_4COOH$, were produced in reasonable amounts. Combining these results we assign the phenoxymethyl-type radical as shown in Figure 9. With a careful measurement we also detected CCl_3• radical in this system. Although involvement of the $CH_3OC_6H_4$• radical was indirectly shown by the observation of the CCl_3• signal in the TREPR experiment and $CH_3OC_6H_4Cl$ in the product analysis, this radical was not directly detected in our TREPR experiment, because the reaction of $CH_3OC_6H_4$• with the solvent CCl_4 is very fast (ca. 0.1 μs).[9c] The absence of the CCl_3• radical just after the laser excitation (Figure 2 and section 3.1) and the lack of the cage-recombination product (section 3.4) in this system indicate that the instant decarboxylation does not occur from the parent MeO-BPO.

Analysis of the temperature dependence of the decay rate constants of the benzoyloxyl radical by the Arrhenius type equation (1) yields the values of $k_0 = 6.6 \times 10^{10}$ s^{-1} and $E_a = 2.0 \times 10^3$ cm^{-1} (5.8 kcal/mol). These values give rise to $k = 6.2 \times 10^7$ s^{-1} at 130 °C, which is in order of magnitude agreement with the value (ca. 1×10^8 s^{-1}) estimated from the CIDNP[2] and spin-trapping[4] experiments. However, as suggested by the LFP studies, the decay rate of the benzoyloxyl radical may not be determined entirely by the decarboxylation rate.[7,8] Careful experiments on the concentration dependence are needed to obtain more accurate rate constants for the decarboxylation in these systems.

4.2.2. Aerated Systems. The CIDEP spectra in the aerated CCl_4 solutions were partly different from those in the deaerated systems. Additional signals with larger g values were obtained and assigned as the peroxyl radicals (section 3). In the case of BPO, as the decay time (ca. 0.2 μs) of the benzoyloxyl radical was the same both in the aerated and deaerated cases, the intermediate radical found in the presence of air would come from the phenyl radical by the following mechanism.

$$C_6H_5COO^{\bullet} \rightarrow C_6H_5^{\bullet} + CO_2$$

$$C_6H_5^{\bullet} \xrightarrow{CCl_4} C_6H_5Cl + CCl_3^{\bullet}$$

$$C_6H_5^{\bullet} \xrightarrow{O_2} C_6H_5OO^{\bullet}$$

In the case of MeO-BPO the (methoxybenzoyl)oxyl radical decays faster (τ 1.2 μs) in the aerated system than in the deaerated one (τ 1.5 μs). The reaction analogous to the case of BPO may occur in the aerated system. The shortening of the decay time

$$CH_3OC_6H_4COO^{\bullet} \rightarrow CH_3OC_6H_4^{\bullet} + CO_2$$

$$CH_3OC_6H_4^{\bullet} + O_2 \rightarrow CH_3OC_6H_4OO^{\bullet}$$

of the intermediate radical might come from the reaction of $CH_3OC_6H_4COO^{\bullet}$ with O_2. The following reaction suggested for the formation of the peroxyl radical[21] might be involved in the present system.

$$2CH_3OC_6H_4COO^{\bullet} + O_2 \rightarrow CH_3OC_6H_4OO^{\bullet} + CH_3OC_6H_4^{\bullet} + 2CO_2$$

5. Conclusion

We have successfully observed and assigned the intermediate radicals produced in the photodecomposition of dibenzoyl peroxides. It is shown that the decarboxylation takes place mostly from the intermediate benzoyloxyl radicals whose lifetimes are in the order of 1 μs at room temperature. It is concluded that the spin states of the intermediate radicals are in thermal equilibrium within 0.5 μs after the laser excitation.

(21) Traylor, T. G.; Clinton, N. *Am. Chem. Soc., Petroleum Chem. Sec.*, Minneapolis, April 1969, p 499.

A New Synthesis of Substituted Furans

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Abstract: A general strategy for the synthesis of five-membered heteroaromatic compounds has been developed which involves the reaction of allenylsilanes with electrophilic species of the general form $Y{\equiv}X^+$. In this report, the feasibility of this strategy is demonstrated by its application in an efficient synthesis of substituted furans. The new annulation is simply achieved by adding allenylsilanes to acylium ions which are generated by the reaction of acid chlorides with aluminum chloride in methylene chloride. A variety of tri- and tetrasubstituted furans are available in good yield by using this regiocontrolled, one-step-annulation method. In addition, an intramolecular variant of this [3 + 2] annulation strategy has been developed to provide efficient access to bicyclic furan derivatives as well.

The status of the *furans*[1] as the most prominent class of heteroaromatic compounds derives from their widespread occurrence in nature and the incorporation of the furan nucleus in the structures of a variety of commercially important pharmaceuticals (e.g. ranitidine) and flavor and fragrance compounds.[2] Equally significant is the role of furan derivatives as versatile synthetic intermediates for the preparation of a wide range of cyclic and acyclic organic compounds.[3] Although numerous synthetic routes to furans are known,[1,4] *single-step* convergent annulation ap-

(1) For general reviews of the chemistry of furans, see: (A) Bosshard, P.; Eugster, C. H. In *Advances in Heterocyclic Chemistry*; Katrizky, A. R., Boulton, A. J., Eds.; Academic Press: New York, 1966; Vol. 7, pp 377-490. (b) Dean, F. M. In *Advances in Heterocyclic Chemistry*; Katrizky, A. R., Ed.; Academic Press: New York, 1982; Vol. 30, pp 167-238. (c) Dean, F. M. In *Advances in Heterocyclic Chemistry*; Katritzky, A. R., Ed.; Academic Press: New York, 1982; Vol. 31, pp 237-344. (d) Dean, F. M.; Sargent, M. V. In *Comprehensive Heterocyclic Chemistry*; Bird, C. W., Cheeseman, G. W. H., Eds.; Pergamon Press: New York, 1984; Vol. 4, Part 3, pp 531-598. (e) Sargent, M. V.; Dean, F. M. In *Comprehensive Heterocyclic Chemistry*; Bird, C. W., Cheeseman, G. W. H., Eds.; Pergamon Press: New York, 1984; Vol. 4, Part 3, pp 599-656. (f) Donnelly, D. M. X.; Meegan, M. J. In *Comprehensive Heterocyclic Chemistry*; Bird, C. W., Cheeseman, G. W. H., Eds.; Pergamon Press: New York, 1984; Vol. 4, Part 3, pp 657-712.

(2) *The Chemistry of Heterocyclic Flavoring and Aroma Compounds*; Vernin, G., Ed.; Ellis Horwood: Chichester, 1982.

(3) For an excellent review, see: Lipshutz, B. H. *Chem. Rev.* **1986**, *86*, 795.

(4) For some recent developments in furan annulation methodology, see: (a) Minami, I.; Yuhara, M.; Watanabe, H.; Tsuji, J. *J. Organomet. Chem.* **1987**, *334*, 225. (b) Jansen, B. J. M.; Peperzak, R. M.; de Groot, Ae. *Recl. Trav. Chim. Pays-Bas* **1987**, *106*, 549. (c) McCombie, S. W.; Shankar, B. B.; Ganguly, A. K. *Tetrahedron Lett.* **1987**, *28*, 4123. (d) Srikrishna, A.; Pullaiah, K. C. *Tetrahedron Lett.* **1987**, *28*, 5203. (e) Hiroi, K.; Sato, H. *Synthesis* **1987**, 811. (f) Davies H. M. L.; Romines, K. R. *Tetrahedron* **1988**, *44*, 3343.

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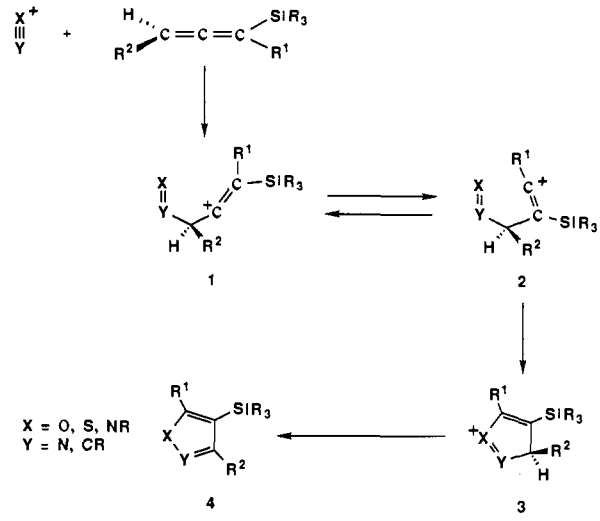
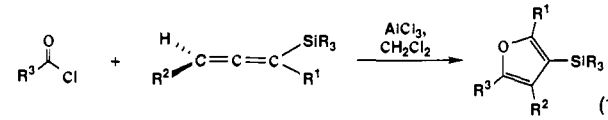
Scheme I



proaches to this system remain extremely rare. Here we report a regiocontrolled [3 + 2] annulation method which provides efficient access to a variety of highly substituted furan derivatives.

Our new furan synthesis is based on the application of allenylsilanes as three-carbon annulation units[5] and illustrates a new and potentially quite general strategy for the synthesis of five-membered heteroaromatic compounds. Electrophilic species of the form $Y{\equiv}X^+$ serve as "heteroallenophiles" in this strategy, combining with allenylsilanes according to the mechanism outlined in Scheme I to produce (in principle) up to six different heterocyclic systems. Thus, addition of the heteroallenophile at C-3 of an allenylsilane produces vinyl cation **1**, which rapidly rearranges to the isomeric vinyl cation **2**. The trialkylsilyl group serves two roles in these initial steps: (a) it directs the regiochemical course of the electrophilic addition (silicon β-effect) and (b) it facilitates the transfer of electrophilic character from the central carbon to the terminus of the three-carbon annulation unit (high migratory aptitude of silyl groups in cationic rearrangements). Cyclization of the vinyl cation **2** next furnishes intermediate **3**, which finally undergoes elimination of H^+ to generate the aromatic heterocycle.

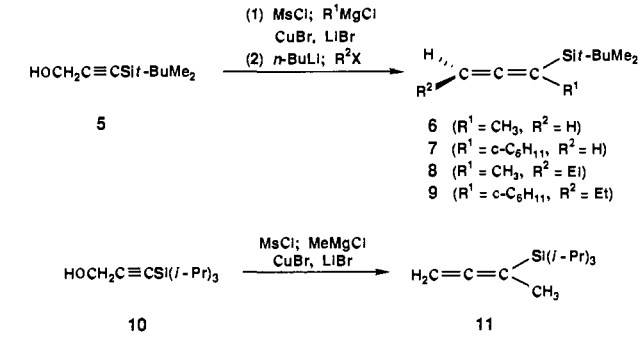
Previously we have demonstrated the feasibility of this heteroaromatic annulation strategy by applying it in an efficient synthesis of substituted isoxazoles;[5c] in that method nitrosonium ion ($N{\equiv}O^+$) functioned as the heteroallenophile. Extension of this strategy to the synthesis of furans requires the deployment of the electrophilic species $RC{\equiv}O^+$ as the allenophile in Scheme I. In fact, we have found that acylium ions generated in situ via the reaction of acyl chlorides with $AlCl_3$ combine smoothly with allenylsilanes in the desired fashion to furnish substituted furans in good yield (eq 1). In a typical reaction, the allenylsilane is



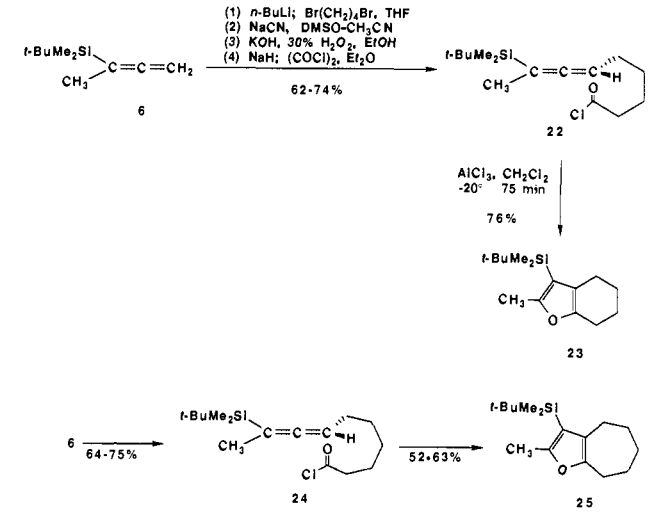
(1)

added to a solution of 1.0 equiv each of $AlCl_3$ and the acyl chloride in methylene chloride at −20 °C, and the resulting orange solution is stirred at that temperature for 1 h. The reaction mixture is then quenched by rapid addition of 1.5 equiv of Et_3N in pentane,[6]

Scheme II



Scheme III



and the furan product is isolated by extractive workup followed by chromatographic purification. Table I summarizes our results.

(*t*-Butyldimethylsilyl)- and (triisopropylsilyl)allenes have proved superior to trimethylsilyl derivatives for this annulation, presumably due to the ability of the larger trialkylsilyl groups to suppress undesirable desilylation reactions. The requisite allenylsilanes are conveniently prepared in one or two steps from 1-trialkylsilyl propargylic alcohols using previously described methods[7] (Scheme II). As expected, allenylsilanes lacking C-1 alkyl groups do not participate in the reaction, since in these cases the desired annulation would require the unfavorable rearrangement of a secondary to primary vinyl cation[8] (see Scheme I). Finally, in reactions involving allenylsilanes which lack C-3 substituents, we have found triisopropylsilyl (TIPS) derivatives to be superior to the corresponding (*tert*-butyldimethylsilyl)allenes. We attribute this fact to the ability of the TIPS group to more effectively shield the adjacent unsubstituted (C-4) position of the furan ring,[9] and thus suppress side reactions involving electrophilic attack at this position.

As indicated by Table I, a variety of acyl chlorides participate in the furan annulation. Relatively sensitive compounds such as the vinylfuran **16** can be prepared provided that $ZnCl_2$ is employed as Lewis acid and the reaction is carried out in the presence of the acid scavenger 2,6-di-*tert*-butyl-4-methylpyridine. Multiple annulations (e.g. entry 6) can be achieved in good yield to generate bis-furan derivatives by employing an inverse addition protocol

(5) For other [3 + 2] annulation methods involving allenylsilanes, see the following. (a) *Cyclopentene Synthesis*: Danheiser, R. L.; Carini, D. J.; Basak, A. *J. Am. Chem. Soc.* **1981**, *103*, 1604. Danheiser, R. L.; Carini, D. J.; Fink, D. M.; Basak, A. *Tetrahedron* **1983**, *39*, 935. Danheiser, R. L.; Fink, D. M. *Tetrahedron Lett.* **1985**, *26*, 2513. Danheiser, R. L.; Fink, D. M.; Tsai, Y.-M. *Org. Synth.* **1988**, *66*, 8. (b) *Dihydrofurans and Pyrrolines*: Danheiser, R. L.; Kwasigroch, C. A.; Tsai, Y.-M. *J. Am. Chem. Soc.* **1985**, *107*, 7233. (c) *Isoxazoles*: Danheiser, R. L.; Becker, D. A. *Heterocycles* **1987**, *25*, 277. (d) *Azulenes*: Becker, D. A.; Danheiser, R. L. *J. Am. Chem. Soc.* **1989**, *111*, 389.

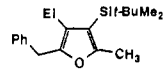
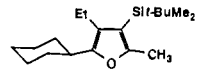
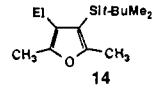
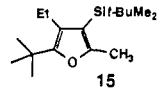
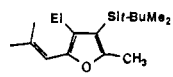
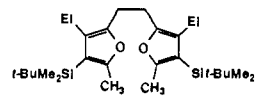
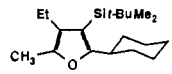
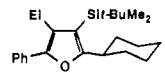
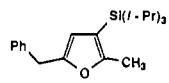
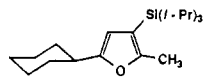
(6) Partial desilylation of the silylfuran annulation products occur when aqueous quenching procedures are employed. To minimize protodesilylation during chromatographic purification, it is advisable to use as eluant petroleum ether containing ca. 1% triethylamine.

(7) The propargylic alcohols **5** and **10** were converted to 1-alkyl-1-(trialkylsilyl)allenes using the general method of Westmijze, H.; Vermeer, P. *Synthesis* **1979**, 390. See also: Danheiser, R. L.; Tsai, Y.-M.; Fink, D. M. *Org. Synth.* **1988**, *66*, 1.

(8) The reaction of 3,3-dimethyl-1-(trimethylsilyl)allene with AcCl and $AlCl_3$ is reported to lead to the formation of 4-methyl-3-[(trimethylsilyl)-methylene]-4-penten-2-one in low yield: Pillot, J.-P.; Bennetau, B.; Dunogues, J.; Calas, R. *Tetrahedron Lett.* **1981**, *22*, 3401.

(9) Corey, E. J.; Rücker, C. *Tetrahedron Lett.* **1982**, *23*, 719.

Table I. Synthesis of Substituted Furans

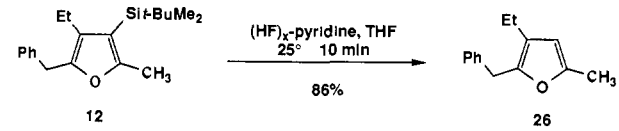
entry	acyl chloride	allenylsilane	furan product[a]	yield, %[b]
1	$PhCH_2COCl$	8	 **12**	71 - 79
2	c-$C_6H_{11}COCl$	8	 **13**	62 - 66
3	CH_3COCl	8	 **14**	68
4	*t*-BuCOCl	8	 **15**	35
5	$Me_2C{=}CHCOCl$	8	 **16**	58
6	succinoyl chloride	8	 **17**	51
7	CH_3COCl	9	 **18**	70
8	PhCOCl	9	 **19**	56
9	$PhCH_2COCl$	11	 **20**	60
10	c-$C_6H_{11}COCl$	11	 **21**	48

[a] IR, UV, ^1H NMR, ^{13}C NMR, and mass spectral data were fully consistent with the assigned structures. Elemental analyses and/or high-resolution mass spectra were obtained for all new compounds. [b] Isolated yields of products purified by column chromatography.

(see the Experimental Section).

The recent development of intramolecular variants of the Diels–Alder reaction and 1,3-dipolar cycloadditions has dramatically expanded the scope and utility of these "classical" annulation methods. The entropic advantage enjoyed by these intramolecular processes makes possible cycloadditions involving otherwise unreactive systems, and these reactions often exhibit greatly enhanced regio- and stereoselectivity as well. We are now pleased to report the first intramolecular examples of our [3 + 2] annulation strategy.[10] The cyclization substrates **22** and **24** required for this study were easily assembled as outlined in Scheme III. Exposure of these allenylsilanes to the action of 1.05–1.1 equiv of $AlCl_3$[11] in CH_2Cl_2 at −20 °C promoted smooth intramolecular annulation to furnish the desired bicyclic furans **23** and **25** in good yield.[12]

In conclusion, we expect that this new annulation strategy should constitute a valuable addition to the methodology for the synthesis of highly substituted furans. It should be noted that the trialkylsilyl substituents in the annulation products have the capacity to facilitate electrophilic substitution reactions at C-3 of the furan ring. On the other hand, if desired, the silyl group can also be easily removed by acid treatment. For example, exposure of silylfuran **12** to pyridinium poly(hydrogen fluoride)[13] in THF at room temperature for 10 min furnished the corresponding desilylated furan **26** in 86% yield.



12 **26**

Further studies are under way in our laboratory to extend this general [3 + 2] annulation strategy to the synthesis of other classes of heteroaromatic compounds.

Experimental Section

Materials. Commercial-grade reagents and solvents were used without further purification except as indicated below. Tetrahydrofuran and diethyl ether were distilled from sodium benzophenone dianion. Acetonitrile, propargyl alcohol, methylene chloride, and dimethyl sulfoxide were distilled from calcium hydride. Methanesulfonyl chloride and all acid chlorides were distilled under argon prior to use. Aluminum chloride was obtained from Fluka Chemical Corp. and stored in sealed ampules under argon prior to use. Copper(I) bromide and lithium bromide were dried by heating at 100 °C (0.01 mmHg) for 24 h.

General Procedures. All reactions were performed in flame-dried glassware under a positive pressure of argon. Reaction mixtures were stirred magnetically unless otherwise indicated. Air- and moisture-sensitive liquids and solutions were transferred via a syringe or cannula into the reaction vessels through rubber septa. Air- and moisture-sensitive solids were handled under an inert atmosphere of argon in a glovebag. Reaction-product solutions and chromatography fractions were concentrated using a Büchi rotary evaporator at ca. 20 mmHg unless otherwise indicated. Residual solvents were removed by evaporation at 0.05 mmHg. Column chromatography was performed by using Baker or E. Merck silica gel (230–400 mesh) or activated basic alumina (Brockmann 1).

3-(*tert*-Butyldimethylsilyl)-2-propyn-1-ol (5). A 2-L, three-necked, round-bottomed flask equipped with a pressure-equalizing addition funnel, a glass stopper, and a reflux condenser fitted with a nitrogen inlet adapter was charged with 2-propyn-1-ol (12.68 g, 0.226 mol) and 400 mL of THF. Ethylmagnesium bromide (360 mL, 1.32 M in THF, 0.475 mol) was added dropwise over 1.5 h, and the addition funnel was rinsed with 10 mL of THF. The reaction mixture was heated at reflux for 8 h, cooled to room temperature, and then treated dropwise over 20 min with a solution of *tert*-butyldimethylsilyl chloride (34.09 g, 0.226 mol) in 250 mL of THF. The resulting dark yellow suspension was heated at reflux for 8 days and then cooled to room temperature and poured into 200 mL of 10% HCl solution. The aqueous layer was separated and extracted with three 100-mL portions of diethyl ether, and the combined organic phases were washed with two 150-mL portions of saturated NaCl solution, dried over $MgSO_4$, filtered, and concentrated to afford ca. 31 g of a yellow oil. Fractional distillation through a 16-cm Vigreux column afforded 29.12 g (76%, 95% pure) of 3-(*tert*-butyldimethylsilyl)-2-propyn-1-ol (**5**) as a waxy solid: bp 68–70 °C (0.3 mmHg); mp 36–38 °C; IR (CCl_4) 3630, 2960, 2940, 2865, 2180, 1475, 1470, 1380, 1365, 1255, 1045, 985, 845, 830, and 685 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 4.25 (s, 2 H), 1.56(s, 1 H), 0.92 (s, 9 H), and 0.09 (s, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 104.6, 88.6, 51.3, 26.0, 16.3, and -4.7; HRMS *m/e* calcd for $C_9H_{18}OSi$ 170.1127, found 170.1128.

3-(Triisopropylsilyl)-2-propyn-1-ol (10). Sequential treatment of 2-propyn-1-ol (1.85 g, 33 mmol) with ethylmagnesium bromide (2.29 M in THF, 30.2 mL, 69 mmol) and then triisopropylchlorosilane (6.36 g, 33 mmol) in 85 mL of THF according to the procedure described above

(10) For a review of intramolecular addition reactions of allylsilanes, see: Schinzer, D. *Synthesis* **1988**, 263.

(11) The success of these intramolecular annulations was found to depend on the source of the aluminum chloride used in the reaction. Material obtained from Fluka Chemical Corp. (used without further purification) gave the best results.

(12) Thus far, our attempts to carry out *intramolecular* annulations employing acyl chlorides branched at the α-position have proceeded in disappointing yield (ca. 20%).

(13) Olah, G. A.; Nojima, M.; Kerekes, I. *Synthesis* **1973**, 779. This reagent is available from Aldrich Chemical Co.

for the preparation of **5** provided 8.5 g of a brown oil. Fractional distillation through a 6-cm Vigreux column afforded 5.96 g (85%, 96% pure) of 3-(triisopropylsilyl)-2-propyn-1-ol (**10**)[14] as a low-melting solid: bp 110 °C (0.9 mmHg); ^{1}H NMR (250 MHz, $CDCl_3$) δ 4.28 (br s, 2 H), 2.28 (br s, 1 H), and 1.08 (s, 21 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 105.7, 86.8, 51.7, 18.5, and 11.2; HRMS *m/e* calcd for $C_{12}H_{24}OSi$ 212.1596, found 212.1597.

1-(*tert*-Butyldimethylsilyl)-1-methylallene (6). A 500-mL, three-necked, round-bottomed flask equipped with a low-temperature thermometer, a rubber septum, and 250-mL pressure-equalizing addition funnel was charged with 3-(*tert*-butyldimethylsilyl)-2-propyn-1-ol (45.3 g, 266 mmol) and 270 mL of THF and then cooled to 0 °C while methylmagnesium chloride (2.8 M in THF, 96 mL, 269 mmol) was added at a rate such that the internal temperature did not rise above 10 °C. Approximately 1.25 h was required for the addition, after which time the gray solution was stirred for another 30 min at 0 °C and then cooled below −70 °C with a dry ice–acetone bath. Methanesulfonyl chloride (30.8 g, 269 mmol) was added via a syringe over 20 min, and the reaction mixture was allowed to warm to room temperature over the course of 2.5 h.

A 2-L, three-necked, round-bottomed flask equipped with a nitrogen inlet adapter and two glass stoppers was charged with copper(I) bromide (40.0 g, 279 mmol) and lithium bromide (24.2 g, 279 mmol). The reaction vessel was evacuated, and the contents were heated briefly with a Bunsen burner several times over the course of 30 min. The vacuum was then replaced by nitrogen and the apparatus was rapidly equipped with a mechanical stirrer and two rubber septa. THF (350 mL) was added, and the resulting green solution containing a small amount of undissolved solid was cooled with an ice bath while methylmagnesium chloride (2.8 M in THF, 96 mL, 269 mmol) was added rapidly via a syringe over 3 min. After 20 min of stirring at 0 °C, the viscous yellow-green suspension was cooled below −70 °C with a dry ice–acetone bath. The solution of the mesylate derivative of 3-(*tert*-butyldimethylsilyl)-2-propyn-1-ol prepared above was cooled below −70 °C and transferred dropwise via a cannula over 70 min to the rapidly stirred suspension of the cuprate reagent. The cold bath was then removed, and the green reaction mixture was allowed to warm to room temperature over 2.5 h. The blue-gray mixture was then poured into a 2-L Erlenmeyer flask containing a magnetically stirred mixture of 400 mL of pentane, 200 mL of water, and 400 mL of saturated NH_4Cl solution. The organic phase was separated and washed successively with two 200-mL portions of saturated NH_4Cl solution, 10 500-mL portions of water, and 100 mL of saturated NaCl solution. The organic phase was dried over Na_2SO_4, filtered, and then concentrated by atmospheric distillation through a 4-cm Vigreaux column. The residual liquid was next carefully distilled through a 4-cm Vigreux column to provide 34.7 g (77%) of the allenylsilane **6** as a colorless liquid (contaminated with up to 9% of 1-(*tert*-butyldimethylsilyl)-1-butyne) as determined by capillary GLPC analysis). Best results (93:7 ratio of allene to acetylene) are achieved by using copper(I) bromide which has been prepared from copper(II) bromide by reduction with sodium sulfite according to the procedure of Keller and Wycoff.[15]

If desired, pure allene can be obtained by employing the following procedure. A 500-mL, one-necked, round-bottomed flask equipped with an argon inlet adapter was charged with the mixture (92:8) of allene and acetylene (8.00 g, 48 mmol) in 100 mL of absolute ethanol. A solution of $AgNO_3$ (12.1 g, 71 mmol) in 114 mL of 3:1 ethanol–water was added in one portion and the clear solution was stirred at room temperature for 12 h. A solution of KCN (21.7 g, 333 mmol) in 37 mL of water was then added in one portion and the resulting mixture was stirred at room temperature for 1 h and then poured into a separatory funnel containing 100 mL each of pentane and water. The aqueous phase was separated and extracted with two 75-mL portions of pentane, and the combined organic phases were then washed with 200 mL of saturated NaCl solution, dried over $MgSO_4$, filtered, and concentrated to provide 6.62 g (90%) of allene **6** as a colorless oil: bp 62–65 °C (30 mmHg); IR (film) 2970, 2950, 2900, 1940, 1480, 1470, 1260, 940, 840, 825, 775, and 680 cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$) δ 4.25 (q, *J* = 3.1 Hz, 2 H), 1.70 (t, *J* = 3.1 Hz, 3 H), 0.89 (s, 9 H), and 0.04 (s, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 210.1, 87.2, 67.3, 26.7, 18.2, 16.7, and −6.3; HRMS *m/e* calcd for $C_9H_{17}Si$ ($M^+ - CH_3$) 153.1100, found 153.1100.

1-(*tert*-Butyldimethylsilyl)-1-cyclohexylallene (7). The mesylate derivative of 3-(*tert*-butyldimethylsilyl)-2-propyn-1-ol was prepared by sequential treatment of the alcohol **5** (1.33 g, 7.8 mmol) in 7.7 mL of THF with methylmagnesium chloride (2.80 M in THF, 2.8 mL, 7.8 mmol) and methanesulfonyl chloride (0.89 g, 7.8 mmol) according to the procedure described above for the preparation of the allene **6**. Reaction of cyclohexylmagnesium chloride (2.0 M in ether, 3.9 mL, 7.8 mmol) with CuBr (1.18 g, 8.2 mmol) and LiBr (0.71 g, 8.2 mmol) in 7.7 mL of THF at −50 °C provided an organocopper reagent which was treated with the mesylate derivative prepared above by using the same procedure employed in the preparation of **6** to afford 1.83 g (99%, 88% pure) of the allene **7** as a colorless oil: IR (film) 2960, 2935, 2860, 1930, 1470, 1460, 1450, 1250, 1020, 855, 840, 825, 810, 770, and 670 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.34 (d, *J* = 2 Hz, 2 H), 1.55–1.80 (m, 6 H), 1.1–1.25 (m, 5 H), 0.89 (s, 9 H), and 0.06 (s, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 209.7, 98.4, 70.0, 38.2, 34.1, 30.2, 26.9, 26.8, 18.5, and −5.9; HRMS *m/e* calcd for $C_{15}H_{28}Si$ 236.1960, found 236.1963.

1-(*tert*-Butyldimethylsilyl)-3-ethyl-1-methylallene (8). A 250-mL, three-necked, round-bottomed flask equipped with two rubber septa and an argon inlet adapter was charged with a solution of allene **6** (90% purity, 5.5 g, 29.4 mmol) in 100 mL of THF and then cooled to −78 °C with a dry ice–acetone bath while *n*-butyllithium (2.48 M, 12.48 mL, 31 mmol) was added rapidly via a syringe. After 20 min, ethyl bromide (3.20 g, 29.4 mmol) was added rapidly dropwise via a syringe and the resulting red mixture was stirred further for 20 min and then allowed to warm to room temperature over 2.5 h. The resulting colorless mixture was diluted with 50 mL of saturated NH_4Cl solution, and the organic phase was separated and washed with 50 mL of saturated NaCl solution, dried over Na_2SO_4, filtered, and concentrated to afford ca. 5 g of a light yellow oil. Column chromatography on silica gel (elution with pentane) gave 4.82 g (84%) of allene **8** as a colorless oil: IR (film) 3130, 2970, 2920, 2860, 2710, 1940, 1470, 1405, 1395, 1365, 1305, 1250, 1110, 1085, 1015, 1010, 940, 885, 830, 778, 730, 680, and 635 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.76 (appar octet, 1 H), 1.96 (AB appar quintet, 2 H), 1.71 (d, *J* = 3 Hz, 3 H), 0.99 (appar t, 3 H), 0.91 (s, 9 H), and 0.04 (s, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 207.1, 89.4, 85.7, 26.8, 21.8, 17.9, 17.5, 14.1, −6.0, and −6.2; HRMS *m/e* calcd for $C_{12}H_{24}Si$ 196.1647, found 196.1647.

1-(*tert*-Butyldimethylsilyl)-1-cyclohexyl-3-ethylallene (9). Sequential treatment of a solution of allene **7** (93% purity, 1.20 g, 4.7 mmol) in 30 mL of THF with *n*-butyllithium (2.48 M in hexanes, 2.0 mL, 5.0 mmol) and ethyl bromide (0.505 g, 0.348 mL, 4.63 mmol) according to the procedure described above for the preparation of **8** afforded 1.043 g (84%) of **9** as a colorless oil: IR (film) 2960, 2930, 2860, 1935, 1465, 1450, 1395, 1365, 1250, 1010, 865, 830, 815, 800, 770, and 670 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.86 (appar t, 1 H), 1.96 (AB appar sextet, 2 H), 1.61–1.81 (m, 6 H), 1.05–1.30 (m, 5 H), 0.99 (appar t, 3 H), 0.89 (s, 9 H), and 0.04 (s, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 206.6, 100.9, 88.4, 39.0, 34.8, 34.1, 30.2, 26.9, 26.2, 21.8, 18.1, 14.0, −5.5, and −5.7; HRMS *m/e* calcd for $C_{17}H_{32}Si$ 264.2273, found 264.2273.

1-(Triisopropylsilyl)-1-methylallene (11). The mesylate derivative of 3-(triisopropylsilyl)-2-propyn-1-ol was prepared by sequential treatment of the alcohol **10** (5.50 g, 26 mmol) in 30 mL of THF with methylmagnesium chloride (2.7 M in THF, 9.6 mL, 26 mmol) and methanesulfonyl chloride (2.97 g, 2.00 mL, 26 mmol) according to the procedure described above for the preparation of the allene **6**. Reaction of methylmagnesium chloride (2.7 M, 9.6 mL, 26 mmol) with CuBr (3.90 g, 27 mmol) and LiBr (2.36 g, 27 mmol) in 60 mL of THF at 0 °C provided an organocopper reagent which was treated with the mesylate derivative prepared above according to the general procedure used in the preparation of allene **6**. Column chromatography on silica gel (elution with pentane) furnished 3.17 g (58%) of **11** as a low-melting solid: IR (film) 2950, 2870, 1935, 1635, 1465, 1385, 1365, 1245, 1110, 1075, 1020, 995, 945, 885, and 815 cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$) δ 4.23 (q, *J* = 3 Hz, 2 H), 1.73 (t, *J* = 3 Hz, 3 H), 1.02–1.3 (m, 21 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 210.6, 84.9, 67.2, 18.6, 17.2, and 11.4; HRMS *m/e* calcd for $C_{13}H_{26}Si$ 210.1804, found 210.1804.

General Procedure for [3 + 2] Furan Annulation. 2-Benzyl-4-(*tert*-butyldimethylsilyl)-3-ethyl-5-methylfuran (12). A 50-mL, one-necked, round-bottomed flask equipped with a three-way argon inlet adapter fitted with a rubber septum was charged with $AlCl_3$ (0.836 g, 6.27 mmol) and 12 mL of CH_2Cl_2 and then cooled to −20 °C while phenylacetyl chloride (0.97 g, 6.27 mmol) was added rapidly via a syringe over ca. 1 min. After 5 min, a solution of allene **8** (95% purity, 1.294 g, 6.26 mmol) in 13 mL of CH_2Cl_2 was added dropwise via a syringe over the course of 1 min. The resulting orange reaction mixture was stirred at −20 °C for 1 h and then quenched by the addition of triethylamine (0.950 g, 9.39 mmol) in 25 mL of pentane. The resulting solution was stirred at room temperature for 10 min, diluted with an additional 25 mL of pentane, and then washed with two 50-mL portions of 10% HCl solution, 50 mL of 3% NaOH solution, 50 mL of water, and 50 mL of saturated NaCl solution. The organic phase was dried over K_2CO_3, filtered, and concentrated to afford ca. 1.5 g of a light yellow oil. Column chromatography on silica gel (elution with 1% triethylamine in petroleum ether) provided 1.39 g (71%) of silylfuran **12** as a colorless oil: IR (film) 2960,

(14) Muchowski, J. M.; Naef, R.; Maddox, M. L. *Tetrahedron Lett.* **1985**, *26*, 5375.

(15) Keller, R. N.; Wycoff, H. P. *Inorg. Syn.* **1946**, *2*, 1.

2930, 2860, 1550, 1495, 1460, 1385, 1360, 1245, 1115, 1070, 1030, 1010, 840, 810, 770, and 700 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 7.20–7.31 (m, 5 H), 3.93 (s, 2 H), 2.43 (q, J = 7.5 Hz, 2 H), 2.30 (s, 3 H), 1.08 (t, J = 7.5 Hz, 3 H), 0.93 (s, 9 H), and 0.31 (s, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.2, 147.1, 139.3, 128.3, 127.0, 126.1, 110.1, 32.0, 26.8, 19.0, 18.5, 16.5, 15.4, and −3.4; UV max (acetonitrile) 228 nm (ϵ = 13 200); HRMS m/e calcd for $C_{20}H_{30}OSi$ 314.2066, found 314.2066.

3-(*tert*-Butyldimethylsilyl)-5-cyclohexyl-4-ethyl-2-methylfuran (13). Reaction of cyclohexanecarbonyl chloride (0.149 g, 1.02 mmol) with allenylsilane **8** (0.199 g, 1.02 mmol) in 4.1 mL of CH_2Cl_2 in the presence of $AlCl_3$ (0.136 g, 1.02 mmol) according to the general procedure afforded 0.200 g (64%) of furan **13** as a colorless oil: IR (film) 2725, 2715, 2675, 1540, 1460, 1450, 1385, 1360, 1250, 1230, 890, 835, 810, 765, and 680 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 2.54 (m, 1 H), 2.34 (q, J = 7.5 Hz, 2 H), 2.26 (s, 3 H), 1.78–1.83 (m, 2 H), 1.68–1.76 (m, 3 H), 1.53–1.61 (m, 2 H), 1.24–1.37 (m, 3 H), 1.05 (t, J = 7.5 Hz, 3 H), 0.87 (s, 9 H), and 0.26 (s, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.0, 153.7, 124.0, 109.6, 35.9, 32.2, 26.7, 22.3, 18.8, 18.5, 17.1, 15.3, 14.0, and −3.3; UV (acetonitrile) 224 nm (ϵ = 8900); MS m/e 306 (M^+). Anal. Calcd for $C_{19}H_{34}OSi$: C, 74.44; H, 11.18. Found: C, 74.63, H, 11.46.

3-(*tert*-Butyldimethylsilyl)-2,5-dimethyl-4-ethylfuran (14). Reaction of acetyl chloride (0.08 g, 1.02 mmol) with allenylsilane **8** (94% purity, 0.213 g, 1.02 mmol) in 4.1 mL of CH_2Cl_2 in the presence of $AlCl_3$ (0.136 g, 1.02 mmol) according to the general procedure afforded 0.165 g (68%) of furan **14** as a colorless oil: IR (film) 2960, 2925, 2830, 1545, 1470, 1390, 1365, 1250, 1225, 1010, 970, 930, 835, 810, 770, and 680 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 2.35 (q, J = 7.5 Hz, 2 H), 2.28 (s, 3 H), 2.18 (s, 3 H), 1.06 (t, J = 7.5 Hz, 3 H), 0.89 (s, 9 H), and 0.26 (s, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.2, 145.3, 125.7, 110.2, 26.7, 19.1, 18.4, 15.9, 15.3, 11.2, and −3.4; UV (acetonitrile) 218 nm (ϵ = 4400); HRMS m/e calcd for $C_{14}H_{26}OSi$ 238.1753, found 238.1753.

2-*tert*-Butyl-4-(*tert*-butyldimethylsilyl)-3-ethyl-5-methylfuran (15). This compound was prepared from allene **8** (0.218 g, 1.11 mmol), pivaloyl chloride (0.134 g, 1.11 mmol), and $AlCl_3$ (0.148 g, 1.11 mmol) according to a modified version of the general procedure in which a solution of the acid chloride in 2.4 mL of CH_2Cl_2 was added dropwise over the course of 6 min to a solution of the allene and $AlCl_3$ in 2 mL of CH_2Cl_2. Column chromatography on silica gel (elution with 1% triethylamine in petroleum ether) furnished 0.108 g (35%) of the furan **15** as a colorless oil: IR (film) 2980, 2960, 2880, 1590, 1550, 1470, 1390, 1370, 1320, 1260, 1220, 1150, 1010, 960, and 690 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 2.47 (q, J = 7.5 Hz, 2 H), 2.25 (s, 3 H), 1.31 (s, 9 H), 1.09 (t, J = 7.5 Hz, 3 H), 0.87 (s, 9 H), and 0.26 (s, 6 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.5, 154.4, 124.3, 110.9, 33.8, 30.0, 26.8, 19.3, 18.7, 17.5, 15.4, and −3.1; HRMS m/e calcd for $C_{17}H_{32}OSi$ 280.2222, found 280.2222.

3-(*tert*-Butyldimethylsilyl)-4-ethyl-2-methyl-5-(2-methylprop-1-enyl)furan (16). A 25-mL, one-necked, round-bottomed flask equipped with a three-way argon inlet adapter was charged with $ZnCl_2$ (0.107 g, 0.79 mmol), 2,6-di-*tert*-butyl-4-methylpyridine (0.154 g, 0.75 mmol) and 4.5 mL of CH_2Cl_2. A solution of allene **8** (0.156 g, 0.79 mmol) in 1.5 mL of CH_2Cl_2 was added rapidly via a syringe followed immediately by a solution of 3,3-dimethylacryloyl chloride (0.088 g, 0.74 mmol) in 3.0 mL of CH_2Cl_2. After 2 h, the resulting deep-blue reaction mixture was quenched with a solution of triethylamine (0.164 mL, 1.18 mmol) in 9.0 mL of pentane. The reaction mixture was further diluted with 20 mL of pentane and then washed with two 20-mL portions of 10% HCl solution, 20 mL of 3% NaOH solution, and 20 mL of saturated NaCl solution. The organic phase was filtered through 1 g of basic alumina (activated, Brockmann I), dried over K_2CO_3, filtered, and concentrated to afford ca. 200 mg of a dark yellow oil. Column chromatography on silica gel (elution with 1% triethylamine in pentane) afforded 0.120 g (58%) of furan **16** as a colorless oil: IR (CCl_4) 2960, 2930, 2860, 1665, 1560, 1460, 1385, 1360, 1260, 1195, 1105, 840, and 680 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 5.91 (br s, 1 H), 2.41 (q, J = 7.5 Hz, 2 H), 2.32 (s, 3 H), 2.05 (s, 3 H), 1.88 (s, 3 H), 1.06 (t, J = 7.5 Hz, 3 H), 0.88 (s, 9 H), and 0.27 (s, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.9, 147.4, 131.9, 128.8, 111.7, 110.4, 27.3, 26.6, 19.9, 19.0, 18.4, 16.3, 15.5, and −3.5; UV (acetonitrile) 202 (ϵ = 15 100) and 279 nm (15 900); HRMS m/e calcd for $C_{17}H_{30}OSi$ 278.2066, found 278.2067.

1,2-Bis(4-(*tert*-butyldimethylsilyl)-3-ethyl-5-methylfur-2-yl)ethane (17). A 25-mL, one-necked, round-bottomed flask equipped with a three-way argon inlet adapter fitted with a rubber septum was charged with $AlCl_3$ (0.211 g, 1.58 mmol) and 2.5 mL of CH_2Cl_2, and cooled to −20 °C while solutions of the allene **8** (94% purity, 0.330 g, 1.58 mmol) in 2.5 mL of CH_2Cl_2 followed by succinoyl chloride (0.116 g, 0.75 mmol) in 1.3 mL of CH_2Cl_2 were rapidly added via a syringe. After 1 h, the resulting red-brown mixture was treated with a solution of triethylamine (0.228 g, 2.25 mmol) in 7 mL of pentane. The reaction mixture was stirred 10 min more at room temperature, diluted with 25 mL of pentane, and then washed with two 25-mL portions of 10% HCl solution, 25 mL of 3% NaOH solution, 25 mL of water, and 25 mL of saturated NaCl solution. The organic phase was dried over K_2CO_3, filtered, and concentrated. Column chromatography on silica gel (elution with 1% triethylamine in petroleum ether) afforded 0.181 g (51%) of the bis-furan **17** as a colorless solid: mp 101–103 °C; IR (CCl_4) 2950, 2920, 2850, 1540, 1460, 1380, 1360, 1250, 1235, 1100, 1060, 1000, 940, and 670 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.81 (s, 4 H), 2.27 (s, 6 H), 2.27 (q, J = 7.5 Hz, 4 H), 0.97 (t, J = 7.5 Hz, 6 H), 0.86 (s, 18 H), and 0.24 (s, 12 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.6, 148.4, 126.3, 110.0, 26.8, 25.3, 18.7, 18.5, 16.4, 15.4, and −3.4; UV (acetonitrile) 229 nm (ϵ = 11 400); MS m/e 474 (M^+). Anal. Calcd $C_{28}H_{50}O_2Si_2$: C, 70.82; H, 10.61. Found: C, 70.63; H, 10.43.

3-(*tert*-Butyldimethylsilyl)-2-cyclohexyl-4-ethyl-5-methylfuran (18). Reaction of acetyl chloride (0.049 g, 0.62 mmol) with allenylsilane **9** (0.165 g, 0.62 mmol) in 2.5 mL of CH_2Cl_2 in the presence of $AlCl_3$ (0.083 g, 0.62 mmol) according to the general procedure afforded 0.134 g (70%) of furan **18** as colorless crystals: mp 84–85 °C; IR (CCl_4) 2940, 2860, 1550, 1460, 1450, 1360, 1260, 1240, 1220, 1140, 1020, and 870 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.57 (m, 1 H), 2.33 (q, J = 7.5 Hz, 2 H), 2.17 (s, 3 H), 1.52–1.84 (m, 7 H), 1.15–1.32 (m, 3 H), 1.05 (t, J = 7.5 Hz, 3 H), 0.89 (s, 9 H), and 0.25 (s, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.8, 145.4, 124.8, 108.2, 39.1, 32.5, 26.8, 26.7, 26.0, 18.9, 17.9, 15.8, 11.4, and −3.0; MS m/e 306 (M^+). Anal. Calcd for $C_{19}H_{34}OSi$: C, 74.44, H, 11.18. Found: C, 74.49; H, 10.92.

3-(*tert*-Butyldimethylsilyl)-2-cyclohexyl-4-ethyl-5-phenylfuran (19). Reaction of benzoyl chloride (0.068 g, 0.48 mmol) with allenylsilane **9** (92% purity, 0.139 g, 0.48 mmol) in 2 mL of CH_2Cl_2 in the presence of $AlCl_3$ (0.065 g, 0.49 mmol) according to the general procedure afforded 0.100 g (56%) of furan **19** as colorless crystals: mp 100–102 °C; IR (CCl_4) 2935, 2860, 1605, 1525, 1490, 1465, 1450, 1380, 1360, 1290, 1255, 1215, 1150, 1070, 1030, 960, 910, and 690 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.21–7.61 (m, 5 H), 2.69 (m, 1 H), 2.65 (q, J = 7 Hz, 2 H), 1.62–1.90 (m, 7 H), 1.25–1.40 (m, 3 H), 1.20 (t, J = 7 Hz, 3 H), 0.92 (s, 9 H), and 0.32 (s, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.3, 146.6, 132.2, 128.4, 128.2, 126.0, 125.1, 110.6, 39.2, 32.5, 26.8, 26.7, 26.0, 19.7, 18.0, 15.4, and −2.8; UV (acetonitrile) 290 nm (ϵ = 18 000); MS m/e 368 (M^+). Anal. Calcd for $C_{24}H_{36}OSi$: C, 78.20; H, 9.84. Found: C, 78.12, H, 10.03.

2-Benzyl-4-(triisopropylsilyl)-5-methylfuran (20). Reaction of phenylacetyl chloride (0.219 g, 1.42 mmol) with allenylsilane **11** (0.300 g, 1.43 mmol) in 5.7 mL of CH_2Cl_2 in the presence of $AlCl_3$ (0.190 g, 1.42 mmol) according to the general procedure afforded 0.280 g (60%) of furan **20** as colorless crystals: mp 63–64 °C; IR (CCl_4) 2955, 2875, 1545, 1495, 1460, 1385, 1235, 1205, 1110, 1075, 1015, 995, 975, and 875 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 7.28 (m, 5 H), 5.85 (s, 1 H), 3.92 (s, 2 H), 2.28 (s, 3 H), 1.25 (septet, J = 7.1 Hz, 3 H), and 1.05 (d, J = 7.1 Hz, 18 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.4, 151.8, 138.7, 128.7, 128.4, 126.2, 112.9, 107.6, 34.3, 18.6, 15.1, and 11.7; UV (acetonitrile) 206 (ϵ = 18 500), 223 (11 700), and 254 (long sh) nm (700); MS m/e 328 (M^+). Anal. Calcd for $C_{21}H_{32}OSi$: C, 76.77; H, 9.82. Found: C, 76.47; H, 9.84.

5-Cyclohexyl-3-(triisopropylsilyl)-2-methylfuran (21). Reaction of cyclohexanecarbonyl chloride (0.157 g, 1.07 mmol) with allenylsilane **11** (0.224 g, 1.06 mmol) in 4.3 mL of CH_2Cl_2 in the presence of $AlCl_3$ (0.143 g, 1.07 mmol) according to the general procedure afforded 0.163 g (48%) of furan **21** as a colorless oil: IR (film) 2940, 2860, 1550, 1460, 1450, 1380, 1200, 1115, 1010, 990, 950, 885, 805, and 780 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.76 (s, 1 H), 2.50–2.60 (m, 1 H), 2.30 (s, 3 H), 1.95–2.07 (m, 2 H), 1.75–1.84 (m, 3 H), 1.65–1.72 (m, 2 H), 1.30–1.40 (m, 3 H), 1.27 (septet, J = 7.4 Hz, 3 H), and 1.06 (d, J = 7.4 Hz, 18 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.4, 155.1, 108.9, 106.9, 37.1, 31.7, 26.2, 26.0, 18.6, 15.1, and 11.7; UV max (acetontrile) 220 (ϵ = 9000) and 275 nm (6900); HRMS m/e calcd for $C_{20}H_{36}OSi$ 320.2535, found 320.2536.

1-(*tert*-Butyldimethylsilyl)-1-methyl-3-(4-bromobutyl)allene (27). A 250-mL, one-necked, round-bottomed flask equipped with a three-way argon inlet adapter fitted with a rubber septum was charged with a solution of 1-(*tert*-butyldimethylsilyl)-1-methylallene (**6**) (3.0 g, 88% purity, 15.7 mmol) in 80 mL of THF and cooled below −70 °C with a dry ice–acetone bath while an *n*-butyllithium solution (1.62 M in hexane, 10.7 mL, 17.3 mmol) was added dropwise over the course of 5 min. After 45 min, 1,4-dibromobutane (5.63 mL, 47.1 mmol) was added dropwise via a syringe over 5 min, and the resulting pink mixture was stirred for 30 min and then allowed to warm to room temperature over 3 h. The crude mixture was added to 10 mL of saturated NH_4Cl solution and then diluted with 60 mL of ether and 20 mL of water. The aqueous phase was extracted with two 60-mL portions of ether, and the combined organic phases were washed with two 30-mL portions of saturated NaCl solution, dried over Na_2SO_4, filtered, and concentrated to give 12.6 g of

a colorless viscous oil. Kugelrohr distillation (105–110 °C, 0.045 mmHg) provided 4.48 g (94%) of allene **27** as a colorless oil: IR (film) 2950, 1950, 1255, 1010, and 840 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 4.67 (appar octet, 1 H), 3.38 (t, J = 6.8 Hz, 2 H), 1.8–2.0 (m, 4 H), 1.68 (d, J = 2.6 Hz, 3 H), 1.48–1.56 (m, 2 H), 0.88 (s, 9 H), and 0.07 (s, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.2, 89.1, 83.1, 33.7, 32.2, 28.2, 27.7, 26.7, 17.8, 17.4, –6.1, and –6.2; MS m/e 304 (M^+, ^{81}Br) and 302 (M^+, ^{79}Br).

1-(*tert*-Butyldimethylsilyl)-1-methyl-3-(4-cyanobutyl)allene (28). A 250-mL, one-necked, round-bottomed flask equipped with a three-way argon inlet adapter fitted with a rubber septum was charged with a solution of the allene **27** (3.05 g, 10.1 mmol) in 30 mL of acetonitrile and 60 mL of dimethyl sulfoxide and then cooled to 0 °C with an ice bath while sodium cyanide (1.33 g, 27.1 mmol) was added in one portion. The mixture was stirred for 5 min at 0 °C, allowed to warm to room temperature over 3 h, and then added to a mixture of 160 mL of pentane and 50 mL of water. The aqueous phase was separated and extracted with two 60-mL portions of pentane, and the combined organic phases were washed with two 2-mL portions of H_2O and 2-mL of saturated NaCl solution, dried over Na_2SO_4, filtered, and concentrated to afford 2.46 g of a colorless oil. Kugelrohr distillation (120–130 °C, 0.3 mmHg) provided 2.39 g (95%) of nitrile **28** as a colorless oil: IR (film) 2940, 2550, 1940, 1010, and 840 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 4.68 (appar octet, 1 H), 2.35 (t, J = 7.1 Hz, 2 H), 2.05 (appar q, 2 H), 1.71 (d, J = 3.0 Hz, 3 H), 1.51–1.76 (m, 4 H), 0.90 (s, 9 H), and 0.04 (s, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.1, 119.6, 89.4, 82.6, 28.5, 27.7, 26.6, 24.8, 17.8, 17.3, 16.9, –6.2, and –6.3; HRMS m/e calcd for $C_{15}H_{27}NSi$ 249.1913, found 249.1910.

8-(*tert*-Butyldimethylsilyl)-6,7-nonadienoic Acid (29). A 500-mL, one-necked, round-bottomed flask equipped with a three-way argon inlet adapter fitted with a rubber septum was charged with a solution of nitrile **28** (2.39 g, 9.6 mmol) in 130 mL of ethanol and 60 mL of 30% H_2O_2, and then cooled to 0 °C while 60 mL of 25% KOH was added slowly via a pipet. The mixture was heated at reflux for 14 h while 80 mL of ethanol was removed by distillation. The remaining solution was then diluted with 350 mL of pentane and acidified to ca. pH 1 with 140 mL of 10% HCl. The aqueous phase was separated and extracted with two 70-mL portions of pentane, and the combined organic phases were then washed with 10 mL of saturated NaCl solution, dried over Na_2SO_4, filtered, and concentrated to provide 2.55 g of a pale yellow oil. Column chromatography on silica gel (elution with 10 to 50% ethyl acetate–hexane) yielded 2.41 g (94%) of acid **29** as a colorless oil: IR (film) 3500–3000 (br), 2950, 1940, 1710, 1250, and 1010 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 11.0–11.5 (br s, 1 H), 4.67 (appar octet, 1 H), 2.35 (t, J = 7.4 Hz, 2 H), 1.95 (AB appar q, 2 H), 1.60–1.72 (m, 2 H), 1.68 (d, J = 3.0 Hz, 3 H), 1.30–1.47 (m, 2 H), 0.87 (s, 9 H), and 0.01 (s, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 207.3, 180.5, 89.0, 83.3, 34.0, 29.1, 28.2, 26.7, 24.2, 17.8 17.4, –6.1, and –6.2.

8-(*tert*-Butyldimethylsilyl)-6,7-nonadienoyl Chloride (22). A 50-mL, one-necked, pear-shaped flask equipped with a three-way argon inlet adapter fitted with a rubber septum was charged with NaH (60% dispersion in mineral oil, 0.221 g, 5.53 mmol). The sodium hydride was washed with three 5-mL portions of ether and then suspended in 7 mL of ether.

A 25-mL, one-necked, pear-shaped flask was charged with a solution of the acid **29** (0.745 g, 2.77 mmol) in 13 mL of ether containing 4 drops of dimethylformamide. This solution was transferred dropwise via a cannula to the suspension of NaH over ca. 1 min. The resulting white suspension of the acid salt was stirred for 30 min at room temperature and then cooled with an ice bath while a solution of oxalyl chloride (3.49 g, 27.5 mmol) in 4 mL of ether was added slowly via a cannula over 2 min. The reaction mixture was allowed to warm to room temperature over 12 h and then transferred via a cannula to a sintered-glass funnel and filtered with the aid of three 10-mL portions of ether. Concentration gave ca. 1 g of a yellow oil. Kugelrohr distillation (95–100 °C, <0.001 mmHg) provided 0.700 g (88%) of acid chloride **22** as a viscous colorless oil: IR (film) 2950, 1950, 1800, 1250, 1010, and 840 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 4.68 (appar octet, 1 H), 2.90 (t, J = 7.6 Hz, 2 H), 1.98 (appar q, 2 H), 1.7–1.8 (m, 2 H), 1.71 (d, J = 2.8 Hz, 3 H), 1.40–1.50 (m, 2 H), 0.89 (s, 9 H), and 0.02 (s, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 207.2, 173.6, 89.3, 82.9, 46.9, 28.4, 28.0, 26.7, 24.5, 17.8, 17.4, –6.1, and –6.3.

3-(*tert*-Butyldimethylsilyl)-2-methyl-4,5,6,7-tetrahydrobenzofuran (23). A 100-mL, one-necked, pear-shaped flask equipped with a three-way argon inlet adapter fitted with a rubber septum was charged with $AlCl_3$ (0.105 g, 0.79 mmol) and 10 mL of CH_2Cl_2 and cooled to –20 °C with a liquid N_2–CCl_4 bath. A solution of the acid chloride **22** (0.209 g, 0.73 mmol) in 3 mL of CH_2Cl_2 was added via a cannula over 5 min, and the resulting pale yellow solution was stirred for 75 min at –20 °C. A solution of triethylamine (0.29 mL, 2.1 mmol) in 15 mL of pentane was then added, and the reaction mixture was allowed to warm to room temperature over 10 min. The resulting mixture was washed with 11 mL of saturated $NaHCO_3$ solution, and the aqueous layer was back-extracted with two 25-mL portions of pentane. The combined organic layers were washed with 6 mL of 3% HCl solution, 6 mL of saturated $NaHCO_3$ solution, and 6 mL of saturated NaCl solution, dried over Na_2SO_4, filtered, and concentrated. Column chromatography on silica gel (elution with hexane) provided 0.139 g (76%) of furan **23** as a colorless oil: IR ($CHCl_3$) 2940, 1250, 1050, and 840 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.55 (appar t, 2 H), 2.40 (appar tt, 2 H), 2.29 (s, 3 H), 1.65–1.82 (m, 4 H), 0.88 (s, 9 H), and 0.22 (s, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.6, 148.2, 122.0, 109.5, 26.5, 24.2, 23.7, 23.1, 23.0, 18.3, 15.0, and –4.0. Anal. Calcd for $C_{15}H_{26}OSi$: C, 71.93; H, 10.46. Found: C, 71.79; H, 10.69.

1-(*tert*-Butyldimethylsilyl)-1-methyl-3-(5-bromopentyl)allene (30). Sequential treatment of allene **6** (86% purity, 2.01 g, 10.3 mmol) with *n*-butyllithium solution (1.63 M in hexanes, 7.76 mL, 12.6 mmol) and 1,5-dibromopentane (8.27 g, 36 mmol) according to the procedure described above for the preparation of allene **27** gave 3.26 g (99%) of **30** as a colorless oil: IR (film) 2950, 1950, 1255, 1010, and 840 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 4.67 (appar octet, 1 H), 3.39 (t, J = 6.8 Hz, 2 H), 1.8–2.0 (m, 4 H), 1.68 (d, J = 2.6 Hz, 3 H), 1.2–1.55 (m, 4 H), 0.89 (s, 9 H), and 0.01 (s, 6 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 207.2, 88.9, 83.4, 33.9, 32.7, 28.9, 28.4, 27.7, 26.7, 17.8, 17.4, –6.1, and –6.2; MS m/e 259 (M^+ – t-Bu, ^{79}Br).

1-(*tert*-Butyldimethylsilyl)-1-methyl-3-(5-cyanopentyl)allene (31). Reaction of bromide **30** (3.19 g, 10.1 mmol) with sodium cyanide (1.32 g, 27.0 mmol) according to the procedure described above for the preparation of **28** furnished 2.42 g (91%) of allene **31** as a colorless oil: IR (film) 2950, 2245, 1940, 1250, 1010, and 840 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 4.66 (appar octet, 1 H), 2.31 (t, J = 7.3 Hz, 2 H), 1.95 (appar quartet, 2 H), 1.68 (d, J = 2.7 Hz, 3 H), 1.3–1.65 (m, 6 H), 0.87 (s, 9 H), and 0.01 (s, 6 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 207.2, 119.7, 89.0, 83.2, 28.8, 28.2, 28.1, 26.7, 25.2, 17.8, 17.4, 17.1, –6.1, and –6.3; MS m/e 248 (M^+ – Me).

9-(*tert*-Butyldimethylsilyl)-7,8-decadienoic Acid (32). Reaction of the nitrile **31** (2.36 g, 8.96 mmol) with KOH and 30% H_2O_2 in aqueous ethanol was carried out using the procedure described above for the preparation of **29**. Column chromatography on silica gel (elution with 10 to 50% ethyl acetate–benzene) yielded 2.30 g (91%) of **32** as a bright yellow oil: IR (film) 3500–3000 (br), 2950, 1940, 1710, 1250, 1010, and 840 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 4.67 (appar octet, 1 H), 2.33 (t, J = 7.5 Hz, 2 H), 1.9–2.0 (br m, 2 H), 1.58–1.68 (m, 2 H), 1.67 (d, J = 3.0 Hz, 3 H), 1.32–1.4 (m, 4 H), 0.89 (s, 9 H), and 0.01 (s, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 207.3, 180.6, 88.8, 83.5, 34.1, 29.3, 28.5, 28.3, 26.7, 24.5, 17.8, 17.3, –6.1, and –6.2. Anal. Calcd for $C_{16}H_{30}O_2Si$: C, 68.03; H, 10.70. Found: C, 67.84; H, 10.50.

9-(*tert*-Butyldimethylsilyl)-7,8-decadienoyl Chloride (24). Sequential treatment of acid **32** (0.598 g, 2.12 mmol) with NaH (60% dispersion in mineral oil, 0.170 g, 4.25 mmol) and oxalyl chloride (2.62 g, 20.6 mmol) according to the procedure described above for the preparation of **22** provided 0.562 g (88%) of **24** as a viscous colorless oil: IR (film) 2950, 1950, 1800, 1250, 1010, and 840 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 4.68 (appar octet, 1 H), 2.88 (t, J = 7.4 Hz, 2 H), 1.9–2.0 (m, 2 H), 1.68–1.75 (m, 2 H), 1.70 (d, J = 3 Hz, 3 H), 1.36–1.42 (m, 4 H), 0.90 (s, 9 H), and 0.03 (s, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 207.2, 173.7, 89.0, 83.3, 47.0, 29.1, 28.2, 27.9, 26.7, 24.9, 17.8, 17.3, –6.1, and –6.2.

3-(*tert*-Butyldimethylsilyl)-2-methyl-5,6,7,8-tetrahydro-4*H*-cyclohepta[*b*]furan (25). Reaction of the allenylsilane **24** (0.350 g, 1.16 mmol) with $AlCl_3$ (0.163 g, 1.22 mmol) in 110 mL of CH_2Cl_2 according to the procedure described above for the preparation of **23** provided 0.160 g (52%) of **25** as a colorless oil: IR (film) 2950, 1540, 1460, 1440, 1250, 1010, and 840 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.65–2.75 (m, 2 H), 2.4–2.5 (m, 2 H), 2.25 (s, 3 H), 1.6–1.8 (m, 6 H), 0.88 (s, 9 H), and 0.24 (s, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.2, 151.3, 125.9, 111.5, 31.0, 28.6, 28.3, 27.1, 26.6, 26.4, 18.2, 15.0, and –3.1. Anal. Calcd for $C_{16}H_{28}OSi$: C, 72.66; H, 10.67. Found: C, 72.85; H, 10.67.

2-Benzyl-3-ethyl-5-methylfuran (26). A 5-dram polyethylene vial fitted with a rubber septum was charged with a solution of the silylfuran **12** (0.324 g, 1.03 mmol) in 1.0 mL of THF. Pyridinium poly(hydrogen fluoride) (3.0 mL, 70% HF) was added in one portion, and the resulting solution was allowed to stir at room temperature for 10 min. The reaction mixture was then carefully added to a stirred, ice-cooled mixture of 35 mL of pentane and 35 mL of saturated $NaHCO_3$ solution. After 5 minutes, ca. 10 g of solid $NaHCO_3$ was added in portions *slowly* until the aqueous phase became saturated. The organic layer was then separated and washed with 20 mL of 10% HCl solution, 20 mL of water, and 20 mL of saturated NaCl solution, dried over K_2CO_3, filtered, and concentrated to afford ca. 0.2 g of a yellow oil. Column chromatography

on silica gel (elution with 1% triethylamine in petroleum ether) provided 0.177 g (86%) of furan **26** as a colorless oil: IR (film) 3080, 3060, 3020, 2960, 2920, 1945, 1800, 1700, 1580, 1500, 1455, 1425, 1385, 1330, 1260, 1235, 1190, 1160, 1105, 1075, 1040, 1000, 980, 920, 885, 800, 750, and 705 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.16-7.30 (m, 5 H), 5.84 (s, 1 H), 3.88 (s, 2 H), 2.34 (q, J = 7 Hz, 2 H), 2.20 (s, 3 H), and 1.11 (t, J = 7 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.9, 146.5, 139.4, 128.4, 128.3, 126.1, 122.5, 107.0, 32.2, 18.1, 15.1, and 13.5; HRMS m/e calcd for $C_{14}H_{16}O$ 200.1201, found 200.1201.

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New Morphologies of Polyacetylene from the Precursor Polymer Polybenzvalene

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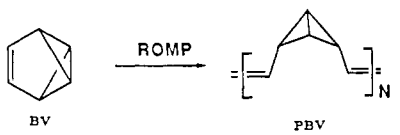
Abstract: The synthesis and properties of the polymer polybenzvalene and its conversion to polyacetylene are presented. This conversion is performed by treating polybenzvalene with Lewis acidic catalysts. The highest quality material was obtained from the isomerization with $HgCl_2$. The polyacetylene (PA) produced by this precursor route has a morphology that is considerably more amorphous than other forms of polyacetylene that have been previously reported. Orientation of the precursor polymer by stretching induced crystallinity and chain alignment as determined by X-ray diffraction. The unoriented PA exhibited a conductivity of 1 Ω^{-1} cm^{-1} with I_2 doping. Materials stretched to elongations of l/l_0 = 2.3 and l/l_0 = 6 displayed conductivities of 13 Ω^{-1} cm^{-1} and 49 Ω^{-1} cm^{-1}, respectively. Block copolymers of polynorbornene and polybenzvalene were produced. These copolymers exhibited no phase separation as determined by DSC. The isomerization of these materials produced a polyacetylene-polynorbornene copolymer which exhibits a dominant X-ray diffraction peak with a d spacing of 4.7 Å. These results indicate that the interchain spacing of the block copolymer is significantly greater than that of the polyacetylene homopolymer due to the intimate mixing of the polyacetylene with the polynorbornene.

The field of conductive polymers has seen considerable study in the last 10 years.[1] Polyacetylene (PA) has received the most extensive investigation[1,2] and has been shown to display conductivities that rival copper.[3] This deceptively simple material is a fundamental cornerstone upon which the field of conductive polymers has been based. Hence, new synthetic routes which can generate new morphologies of PA should be pursued. Conductive polymers including PA are often insoluble and infusible materials with low tensile strength. Thus, the manipulation of these materials into useful shapes and morphologies is limited. The morphology of many conductive polymers is fixed in the polymerization and is not easily modified.[1] One solution to the problems encountered in processing conductive polymers has been to use a processable precursor polymer which can be transformed into a conductive polymer. Precursor routes to conductive polymers have successfully produced high molecular weight materials with high conductivities and oriented morphologies.[4] The most relevant precursor method here is the synthesis of PA by Feast.[4a] PA

Scheme I



synthesized by Feast's method has been called "Durham PA" and has seen considerable study.[5] However, known precursor methods have been limited to processes which involve the extrusion of molecular fragments. In some cases, this extrusion involves over half the mass of the precursor polymer. Extrusions such as these restrict the processing of these materials into large shapes and prohibit processing by methods such as mold injection. In addition, materials produced by extrusion processes often have a porous structure which is undesirable for some applications. Thus, the development of nonextrusive precursor methodologies for the synthesis of conductive polymers is worth pursuing.

A strategy based on intramolecular, electrocyclic rearrangements may successfully meet the nonextrusive criterion.[6] In this scheme, olefins are masked by incorporating them into ring systems. The resulting saturated centers of the ring act to make the polymer backbone nonplanar and more flexible, thus imparting greater solubility to the polymer. Demonstrating this idea, we recently reported preliminary results regarding a new synthesis of PA from the precursor polymer polybenzvalene (PBV).[7] We report herein a more detailed account of this process and the production of new morphologies of PA using this precursor method.

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