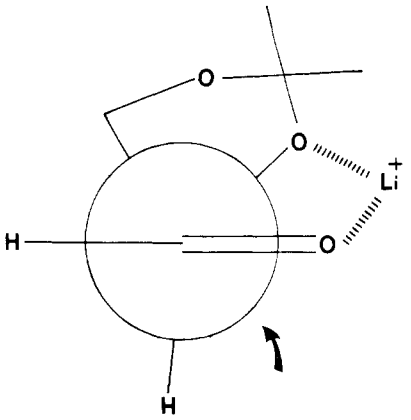

Figure 1.

was added methyl 3-(dimethylamino)propanoate **2** (2.0 g, 15.3 mmol). To the resulting milky reaction mixture was slowly added with stirring, 15 min later, a solution of isopropylidene-D-glyceraldehyde (2.0 g, 15.3 mmol) in THF (10 mL). After another 15 min at −78 °C, the resulting mixture was quenched with water (10 mL). After the aqueous layer was extracted with ethyl acetate, the combined THF and ethyl acetate layers were dried over magnesium sulfate and the solvent was removed. The NMR spectrum of the crude residue showed complete disappearance of the aldehydic hydrogen. Crude **3** (3.97 g, 15.3 mmol) was dissolved in ether (30 mL). Methyl iodide (20 mL) was added and the solution was stirred at room temperature for 2 h. The resulting precipitated salt was filtered and dissolved in a saturated aqueous sodium bicarbonate solution (50 mL), and ethyl acetate (50 mL) was added. After stirring at room temperature for 30 min, the organic layer was separated and the aqueous layer extracted with 3 × 20 mL of ethyl acetate. The combined organic layers were dried over $MgSO_4$, concentrated, and "flash" chromatographed on a silica gel column (eluent, ether–hexane 1:1), affording pure **4** (2.18 g, 10 mmol), 66% yield): $[\alpha]_D$ = −17.0° (*c* 1.50, acetone); IR ($CHCl_3$) 3473 (OH), 1719 (C=O), 1634 (C=C) cm^{-1}; ^1H NMR ($CDCl_3$) 1.35 (s, 3 H), 1.44 (s, 3 H), 2.98 (d, 1 H, J = 5.09, D_2O exchangeable), 3.79 (s, 3 H), 3.92 (d, 2 H), 4.34 (dt, 1 H), 4.53 (m, 1 H), 5.99 (dd, 1 H, J = 1.27 and J = 1.29), 6.36 (m, 1 H). Anal. Calcd for $C_{10}H_{16}O_5$: C, 55.55; H, 7.45. Found: C, 55.56; H, 7.27.

2-Deoxy-2-*C*-methylene-D-*erythro*-pentono-1,4-lactone (5). To compound **4** (1.0 g, 4.6 mmol) cooled to 0 °C was added trifluoroacetic acid (18 mL) and water (2 mL). Immediately afterward, stirring was started and the temperature was allowed to rise over 2 h to room temperature. Evaporation to dryness afforded a solid which was purified by flash chromatography on silica gel (eluent, ethyl acetate): yield 51% (0.34 g, 2.3 mmol); mp 66 °C; $[\alpha]_D$ −91.3 (*c* 1.10, methanol); IR (KBr) 3365 (OH), 1766 (C=O), 1651 (C=C) cm^{-1}; ^1H NMR (D_2O) 4.24 (m, H_4), 4.44 and 4.51 (AB part of an ABX spectrum, H_5 and $H_{5'}$, $J_{5,4}$ = 2.0 and $J_{5',4}$ = 3.3), 4.72 (ddd, H_3, $J_{3,2} = J_{3,2'} = J_{3,4}$ = 2.0), 6.16 (dd, $H_{2'}$, $J_{2,2'}$ = 2.0), 6.62 (dt, H_2, $J_{2,4}$ = 1.5). Anal. Calcd for $C_6H_8O_4$: C, 50.00; H, 5.55. Found: C, 49.83; H, 5.88.

Note Added in Proof: After this manuscript was accepted, a similar approach for the stereoselective synthesis of α-methylene-β-hydroxy-γ-acetoxy esters was described: Banfi, L.; Bernardi, A.; Colombo, L.; Gennari, C.; Scolastico, C. *J. Org. Chem.* **1984**, *49*, 3784.

Registry No. **1**, 15186-48-8; **2**, 3853-06-3; **3**, 93684-93-6; *threo*-**4**, 93684-94-7; *erythro*-**4**, 93714-49-9; **5**, 74948-84-8; CH_3I, 74-88-4.

Gas-Phase Thermal Rearrangements of Potential Vinylidene Precursors to Silylbenzofurans and Silylbenzopyrans

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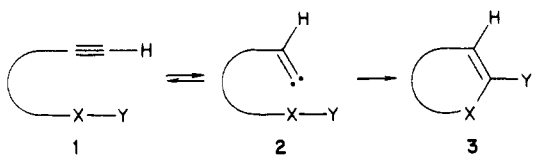
In an attempt to utilize the considerable migratory aptitude of silicon in the synthesis of 3-silylbenzofurans, the flash vacuum pyrolysis (FVP) of *o*-[(trimethylsilyl)ethynyl]phenol was found to provide not only the furan expected from vinylidene cyclization but two isomers resulting from initial 1,5-hydrogen migration from oxygen to form an intermediate allenyl ketone. FVP of 2-(trimethylsilyl)-4,5-dihydrofuran produced an unprecedented gas-phase reductive elimination to a vinylidene. *o*-Ethynyl- and *o*-propynylanisoles did not afford benzopyrans through vinylidene/C-H(Me) insertion but underwent radical transformations. However, *o*-[(trimethylsilyl)-ethynyl]anisole unexpectedly extruded Me_2Si to form 2-ethylbenzofuran as the only product. Various mechanisms for this remarkable decomposition are considered. The acyclic analogue 1-(trimethylsilyl)-4-methoxybut-1-yn-3-ene pyrolytically extruded not Me_2Si but carbon monoxide! This is rationalized as proceeding through an initial 1,5-methyl migration from oxygen to carbon.

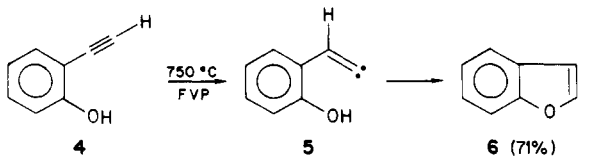
The thermally induced isomerization of acetylenes to vinylidenes (**1** ⇄ **2**), discovered by Brown[1] in 1974, has



1 **2** **3**

been utilized via intramolecular trapping (**2** → **3**) in the synthesis of bicyclic enones by Dreiding[2] and most recently by us[3] in the synthesis of unsaturated silacycles.

Bloch[4] has reported that flash vacuum pyrolysis (FVP) of (*o*-hydroxyphenyl)acetylene (**4**) at 800 °C results in quantitative conversion to benzofuran **6**, and this is reasonably interpreted as proceeding through the intermediacy of vinylidene **5**. In our hands, FVP of **4** at 750 °C



4 **5** **6** (71%)

(1) Brown, R. F. C.; Eastwood, F. W.; Harrington, K. J.; McMullen, G. L. *Aust. J. Chem.* **1974**, *27*, 2393.

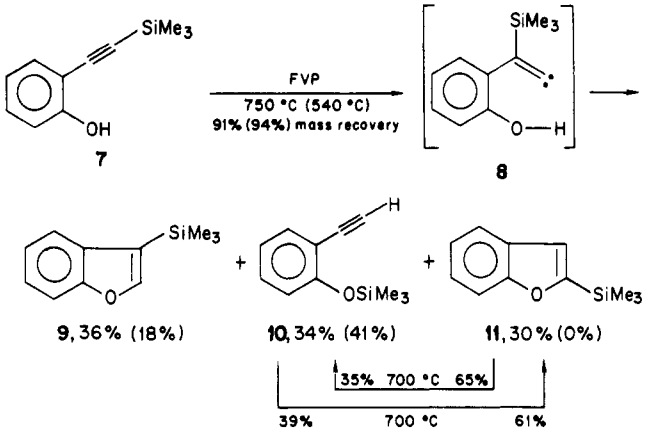
(2) (a) Manzardo, G. G. G.; Karpf, M.; Dreiding, A. S. *Helv. Chim. Acta* **1983**, *66*, 627. (b) Huguet, J.; Karpf, M.; Dreiding, A. S. *Helv. Chim. Acta* **1982**, *65*, 2413. (c) Karpf, M.; Dreiding, A. S. *Helv. Chim. Acta* **1981**, *64*, 1123. (d) Karpf, M.; Dreiding, A. S. *Helv. Chim. Acta* **1979**, *62*, 852.

(3) Barton, T. J.; Groh, B. L., submitted for publication.

(4) Bloch, R.; Orvane, P. *Tetrahedron Lett.* **1981**, *22*, 3597.

0022-3263/85/1950-0158$01.50/0

Scheme I



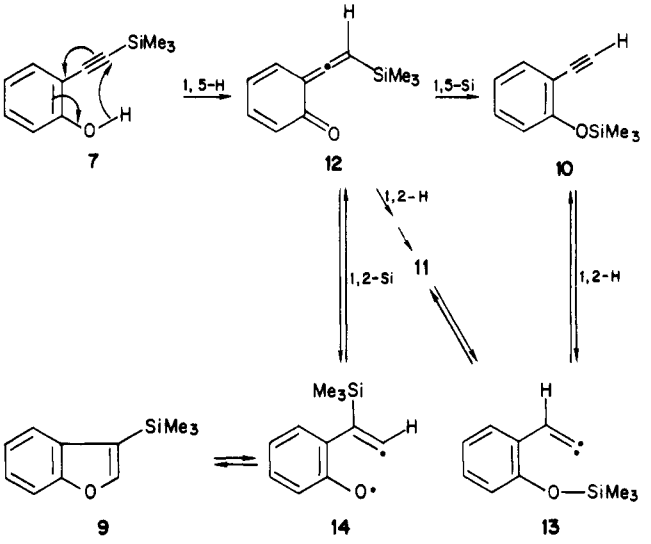
also produced **6** as the sole observable product, but in 71% yield with 71% mass recovery.

As the benzofuran ring system occurs frequently in nature,[5] we felt that this nucleus provided a worthy target to include in our program of silyl migrations on π-frameworks. Thus, the original impetus for this study was to utilize the trimethylsilyl unit as the migrating group in vinylidene production so as to form 3-silylbenzofurans. The silyl group could then allow a variety of synthetic transformations at the synthetically perverse[5] 3-position. To this end, *o*-[(trimethylsilyl)ethynyl]phenol (**7**) was subjected to FVP at 750 °C (Scheme I). The desired 3-(trimethylsilyl)benzofuran (**9**) was indeed a major product but was unexpectedly accompanied by silyl ether **10** and 2-(trimethylsilyl)benzofuran (**11**) (relative yields of 36%, 34%, and 30%; mass recovery 91%). It could be demonstrated that this product mixture did not simply arise from isomerization of initially formed **9** since **9** was unaffected at 700 °C and even at 800 °C produced **10** and **11** in only 21% and 10%, respectively. Therefore, even though **9** can eventually intersect with the energy surface of **10** and **11**, it is apparently not their sole source in the FVP of **7**. Furthermore, **11** is not a primary product in this pyrolysis since at 540 °C no **11** is formed even though quite significant yields of **9** and **10** (18% and 41%) are observed. That **11** is reversibly formed from **10** was demonstrated by the independent FVP of **10** and of **11** at 700 °C to afford in each case a mixture of the two and none of **9**.

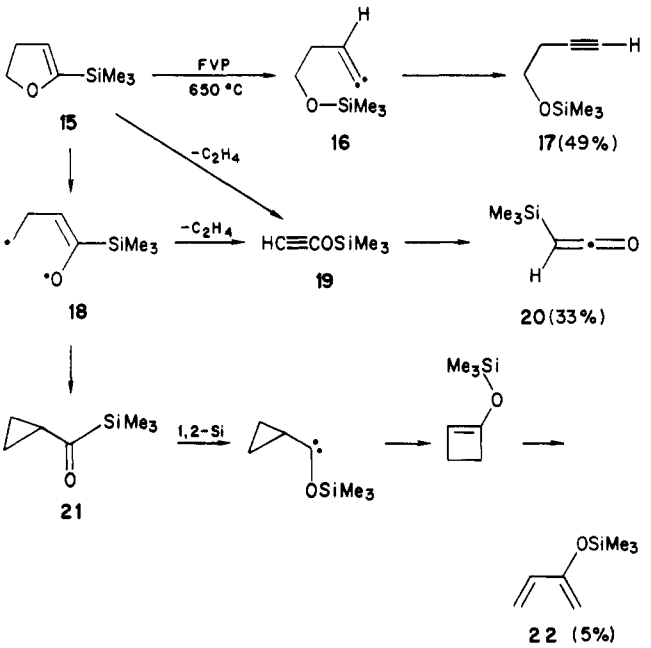
Thus, in the FVP of **7**, there is an operative pathway that leads to silyl ether **10**, which then equilibrates with the 2-silyl isomer **11**. We propose that this second route is initiated by 1,5-hydrogen migration from oxygen to carbon to afford allenyl ketone **12** which then undergoes a 1,5-silyl shift to oxygen to rearomatize and produce **10** (Scheme II). The presence of this second mechanistic pathway is, of course, not revealed in the thermolysis of **4** since the same product, **6** is formed by either route. As to the isomerization of **10** to **11**, this can be rationalized by 1,2-hydrogen rearrangement to form vinylidene **13** which can insert into the Si–O bond to produce **11**.

Recognition of the intermediacy of allenyl ketone **12** introduces the interesting possibility that *both* **10** and **9** arise from this single intermediate and that vinylidene **8** is never involved in the FVP of **7**. Thus, **12** could (a) undergo a 1,5-silyl shift to form **10**; (b) undergo a 1,2-hydrogen shift to produce a diradical which would close to **11**; or (c) undergo a 1,2-silyl shift to yield diradical **14** leading to **9**. Lastly, it is noted that at higher temperatures the 3-silyl isomer **9** may enter this energy surface by homolytic C–O bond cleavage followed by a 1,2-shift in diradical **14** to afford **11**.

Scheme II



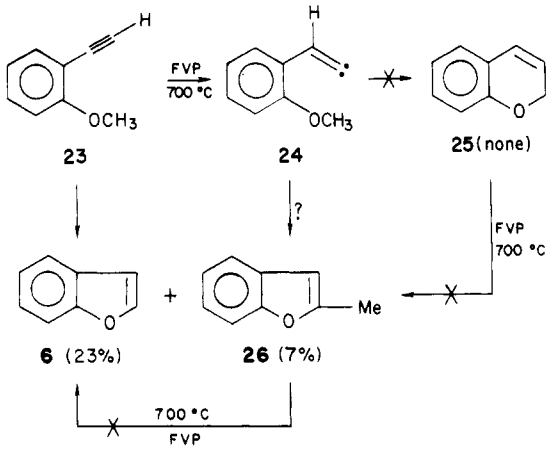
Scheme III



The suggestion that 2-silylbenzofuran **11** isomerizes to vinylidene **13** (on the way to **10**) would represent what is to our knowledge the first example of a gas-phase reductive elimination to form a vinylidene. Supportive evidence for the proposed isomerization of **11** to **13** was sought through the pyrolysis of the model system, 2-(trimethylsilyl)-4,5-dihydrofuran (**15**). It was anticipated that **15** would undergo rearrangement to vinylidene **16** and collapse to 4-(trimethylsiloxy)-1-butyne (**17**). Indeed, FVP (650 °C) of **15** did produce **17** as the major product in 49% yield. However, a second major product, (trimethylsilyl)ketene (**20**), was formed in 33% yield along with a small amount (5%) of 2-(trimethylsiloxy)-1,3-butadiene (**22**) (Scheme III). Both of these products, **20** and **22**, can be rationalized as originating from initial C–O bond homolysis to produce

(5) (a) Dean, F. M. "Naturally Occurring Oxygen Ring Compounds"; Butterworths: London, 1973; Chapter 5. (b) Cogniant, P.; Cogniant, D. In "Advances in Heterocyclic Chemistry"; Katritzky, A. R., Boulton, A. J., Ed.; Academic Press: New York, 1975; Vol. 18, pp 337–482. (c) Mostafa, A. In "The Chemistry of Heterocyclic Compounds: Benzofurans", Weissberger, A., Taylor, E. C., Ed.; Wiley Interscience: New York, 1974; Vol. 29.

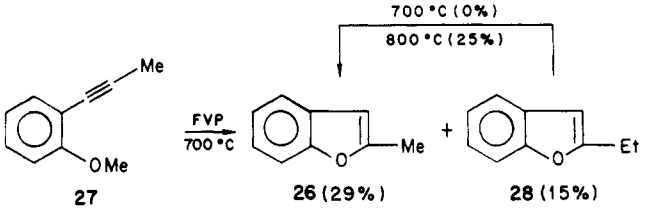
Scheme IV



diradical 18. Extrusion of ethylene from 18 would either form ketene 20 or (trimethylsiloxy)ethyne 19 which is known[6] to thermally rearrange to 20. Alternatively, 18 could close to form cyclopropyl ketone 21, and this is in fact the major process observed in the thermolysis of unsubstituted 2,3-dihydrofuran.[7] However, silyl ketone 21 can now undergo a 1,2-silyl shift to oxygen[8] to form a carbene which would be expected to ring expand[9] and open to the minor product 22.

We next attempted to extend the vinylidene cyclization to the synthesis of benzopyrans through the pyrolysis of *o*-ethynylanisole (23) (Scheme IV). Quite surprisingly, FVP of 23 at 700 °C produced none of the desired pyran 25, which was anticipated from intramolecular C–H insertion in vinylidene 24. Instead, benzofuran (6) (23%) was the major volatile product and was accompanied by 2-methylbenzofuran (26) in 7% yield. The possibility that benzopyran 25 was formed but rearranged to furan 26 appears to be eliminated by the observation that 25 was found to be largely unaffected by FVP at 700 °C. Other than recovered 25 (77%), there were eight very minor pyrolysis products which GCMS analysis revealed not to be either 6 or 26.

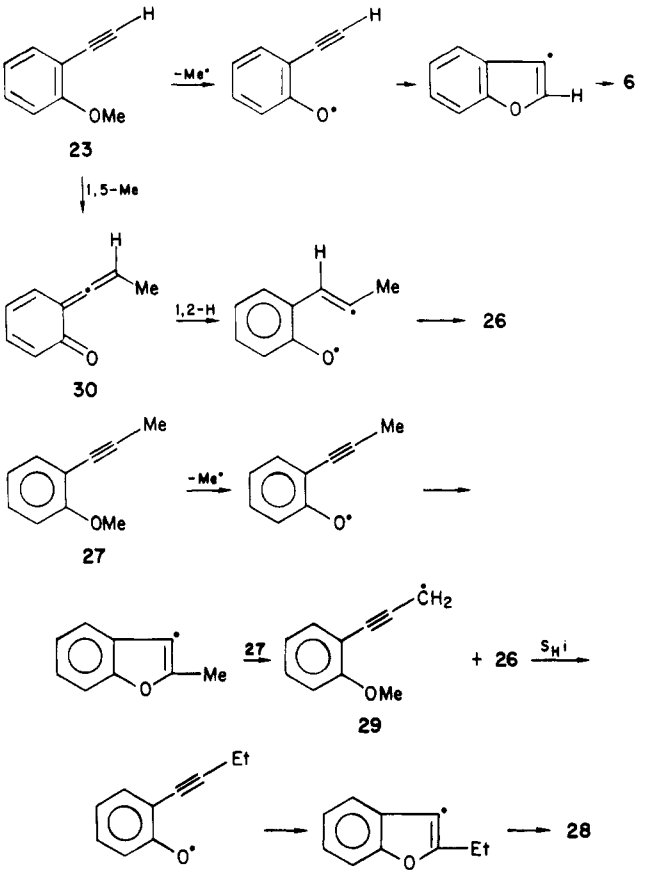
Similar results were obtained in the FVP (700 °C) of *o*-(1-propynyl)anisole (27), which afforded 26 (29%) and



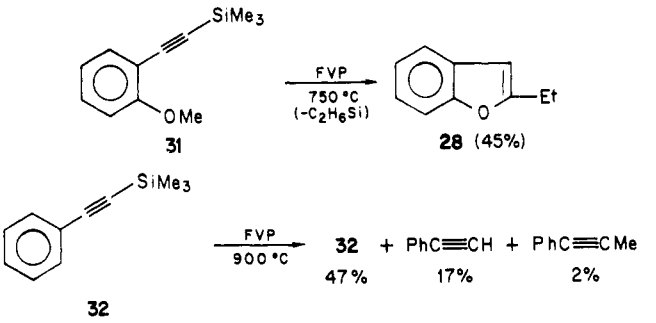
2-ethylbenzofuran (28) (15%) and no benzopyrans. Although pyrolysis of 28 at 700 °C produced no 26, at 800 °C a 25% yield of 26 was realized. Thus, it is possible that initially formed, thermally activated ("hot") 28 is a source of 26 in the pyrolysis of anisole 27 via C–C homolysis and loss of methyl radical.

Since 2-methylbenzofuran (26) is demonstrably not a source of benzofuran (6), there appear to be at least two operative pathways in the thermolysis of anisole 23. Formation of 6 presumably arises from homolytic loss of $\cdot CH_3$, followed by radical cyclization (Scheme V). Loss

Scheme V



Scheme VI

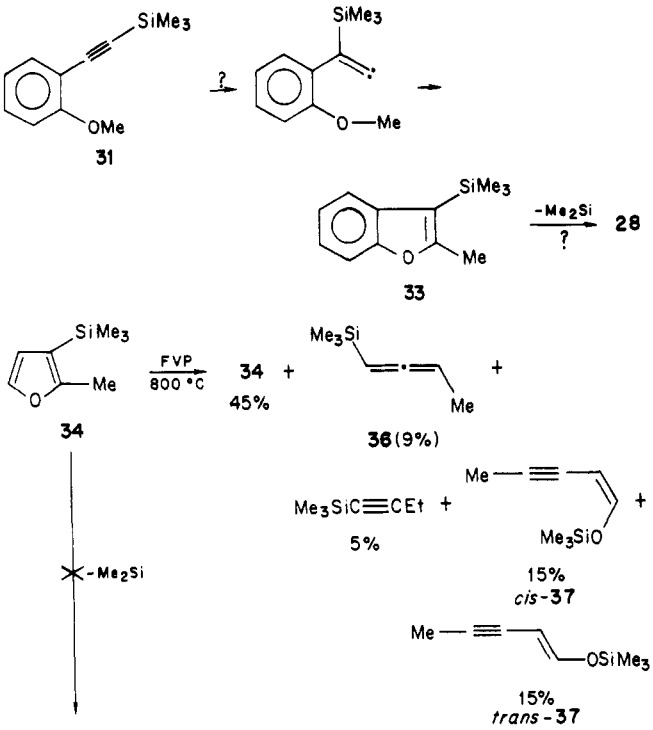


of methyl radical from anisole is reported[10] to produce phenol in 52% yield at 640 °C in a flow pyrolysis. Indeed, such a process will also account for the formation of 26 in the FVP of 27, although O–C insertion by vinylidene 24 cannot be ruled out. At any rate, the predominant pathway for both anisoles 23 and 27 seems to be initiated by homolytic cleavage. Radical rearrangement would appear to be the only explanation for the formation of 2-ethylbenzofuran (28). We suggest that this occurs by a migration of methyl in radical 29 (an S_{Hi} reaction) followed by cyclization. Thus, the only product which cannot be readily accounted for by radical processes is 2-methylbenzofuran (26) in the FVP of 23. We propose that this arises by an initial 1,5-sigmatropic migration of methyl from oxygen to form allenyl ketone 30, rearomatization via a 1,2-hydrogen shift, and diradical closure to 26 (Scheme V).

Although benzopyran formation was not realized in the pyrolysis of 23, it was hoped that the usual superior mi-

(6) Shchukovskaya, L. L.; Kol'tsov, A. I.; Lazarev, A. N.; Pal'chik, R. I. *Dokl. Akad. Nauk SSSR* **1968**, *174*, 892.
(7) Wilson, C. L. *J. Am. Chem. Soc.* **1947**, *69*, 3002.
(8) Brook, A. G.; Bassindale, A. R. In "Organic Chemistry", Essay No. 9, DeMayo, P., Ed.; Academic Press: New York, 1980.
(9) Friedman, L.; Schechter, H. *J. Am. Chem. Soc.* **1960**, *82*, 1002.
(10) Freidlin, L. Kh.; Balandin, A. A.; Nazarova, N. M. *Izv. Akad. Nauk SSSR* **1949**, 102.

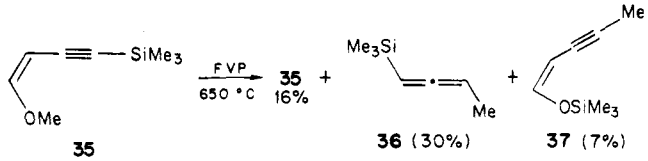
Scheme VII



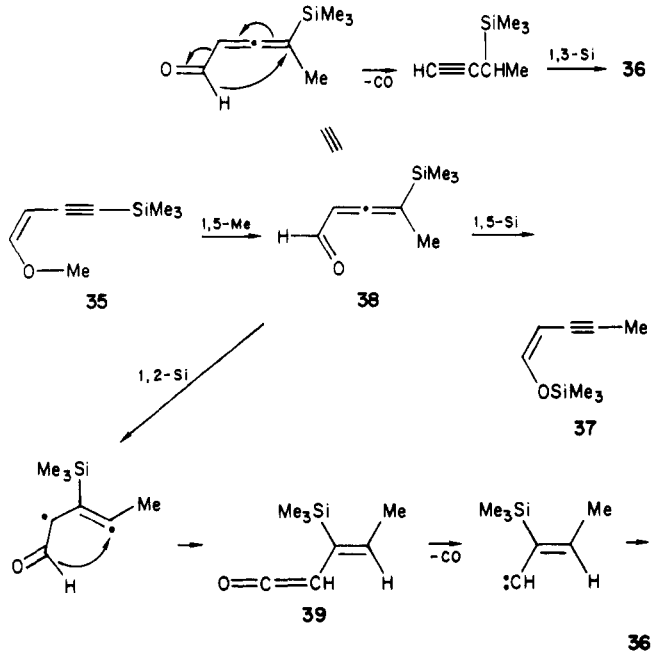
gratory aptitude of silicon[8] relative to hydrogen might allow the desired transformation of an ethynylanisole to a benzopyran. Thus, *o*-[(trimethylsilyl)ethynyl]anisole (**31**) was subjected to FVP at 750 °C (Scheme VI). Only a single volatile product was observed, 2-ethylbenzofuran (**28**) in 45% yield. The totally unanticipated formation of **28** corresponds to a remarkable extrusion of the elements of Me_2Si. The possibility that this transformation is initiated by a reductive elimination of dimethylsilylene to form anisole **27** would appear to be ruled out not only by our observation (vide supra) that FVP of **27** produces **26** as the major product but also by the fact that phenyl(trimethylsilyl)acetylene (**32**) does not significantly decompose before 900 °C, at which temperature only 2% of 1-phenylpropyne is observed. Therefore, the unassisted reductive elimination of Me_2Si: cannot be invoked under the FVP conditions utilized.

Next considered was the possibility that **31** isomerized by the desired 1,2-silyl shift, with the resulting vinylidene inserting into the O–Me to produce a benzofuran **33** which ultimately decomposed to **28** (Scheme VII). Attempts to synthesize **33** in order to test this seemingly remote possibility were unsuccessful. However, we consider this route very unlikely since we find the nonbenzannulated analogue, furan **34**, to only partially decompose at 800 °C to give only products *retaining* the trimethylsilyl group. Thus, there is no reason to suspect that **33** would eliminate Me_2Si.

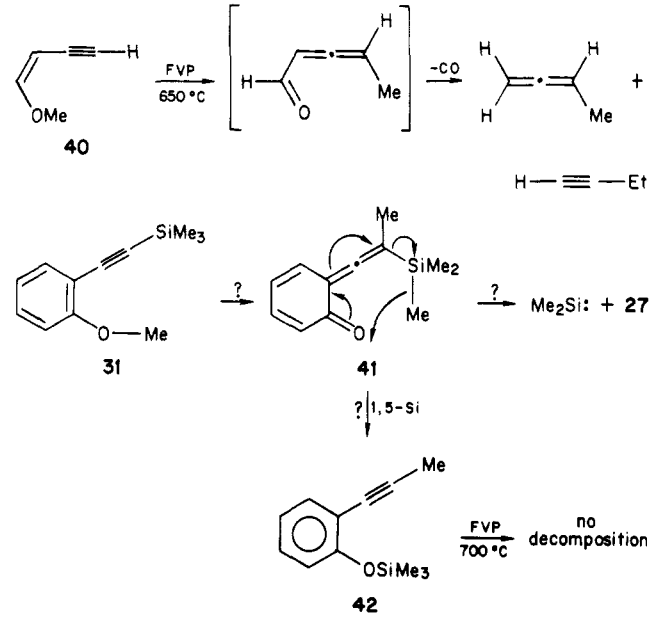
Finally, we turned to an acyclic model of **31**, enyne **35**, in hopes of gaining insight into the mode of decomposition of **31**. This was not to be, as instead of Me_2Si loss, the major product from the 650 °C FVP of **35**, allene **36**, results from loss of carbon monoxide! The only other volatile product observed was one of isomerization, siloxy enyne **37**, where the methyl and trimethylsilyl of **35** have exchanged positions. Both the isomerization and the unanticipated extrusion of CO can be explained by an initial 1,5-sigmatropic methyl migration, as suggested for the isomerization of **23** to **30** in Scheme V. Thus, isomerization of **35** (Scheme VIII) to allenylaldehyde **38** leads to product **37** via a 1,5-silyl shift to oxygen. Although decarbonylation of **38** could lead to an alkyne that would be expected to isomerize to allene **36**, an alternate route involving 1,2-silyl migration, rearrangement of the resulting diradical to ketene **39**, decarbonylation, and rearrangement to **36** appears equally likely at this time.



Scheme VIII



Scheme IX



The surprising decarbonylation of **35** is not dependent upon the presence of silyl substitution since we find that the major volatile products from a 650 °C FVP of the parent methoxy enyne **40** are 1-butyne and 1,2-butadiene (Scheme IX). Thus, 1,5-methyl migration on this electronic framework appears to be a general process. It is difficult to believe that this route is not also operative in the puzzling pyrolysis of silylanisole **31**, and one can envision extrusion of Me_2Si from the resulting allenyl ketone

intermediate **41**. However, the absence of 2-methylbenzofuran (**26**) in the FVP of **31** makes this a bothersome explanation since **26** is the major product of the FVP of **27**. Also, one would have expected **41** to rearrange to acetylene **42** via a 1,5-silyl shift, as proposed for the transformation **38** → **37**. No **42** is found in the FVP of **31**, and **42** was found to be perfectly stable in FVP at 700 °C. Even at 800 °C most of **42** is not decomposed or rearranged. Clearly, it will be necessary to perform definitive labeling studies before further comment on this intriguing transformation can be made.

Experimental Section

General Methods. Routine ^{1}H NMR (60 MHz) spectra were recorded on a Varian EM-360A or L spectrometer. High-resolution ^{1}H NMR (300 MHz) spectra were recorded on a Nicolet NT-300 spectrometer. ^{13}C NMR spectra were recorded on Nicolet NT-300 (75.5 MHz) or JEOL FX90Q (22.5 MHz) spectrometers. All chemical shifts are reported as parts per million (δ scale) from tetramethylsilane and were taken in $CDCl_3$ unless otherwise noted. Mass spectra (MS) were recorded on a Finnigan 4000 (GCMS) or AEI-MS-902 operating at 70 eV and are reported as m/e (relative intensity) unless otherwise indicated. IR spectra were recorded on a Beckman IR 4250 or an IBM 98 FTIR spectrophotometer and were taken as neat samples except as indicated otherwise.

Gas chromatographic (GC) analyses were performed on a Hewlett-Packard 5790A fitted with a nonpolar 12.5-m capillary column. Preparative GC was performed on a GOW MAC 550P or a Varian 1700 using columns as specified within the experimental procedures.

Yields were determined by GC using internal standards after determination of the appropriate response factors or by ^{1}H NMR using internal standards.

Elemental analyses were performed by Galbraith Laboratories, Inc., or by Mic Anal Organic Microanalysis.

General Conditions for Flash Vacuum Pyrolyses (FVP). All samples were distilled or sublimed from a bath maintained at a temperature allowing slow introduction (ca. 80 mg/h) of the sample into a horizontal, quartz tube packed with quartz chips and heated with an electric tube furnace. The heated zone of the quartz tube was ca. 1.8 cm × 30 cm. Pyrolysates were collected in a cold trap cooled with liquid N_2. Pressures were measured by an ionization gauge behind two liquid N_2 traps and, therefore, do not accurately reflect the actual pressure in the reaction zone. For the FVP's of compounds **7**, **9**, **10**, and **11**, ratios of products as determined by NMR are reported for ease of comparison. Yields obtained by NMR were found to be identical with values obtained by adjusting the ratios in accordance with mass recoveries.

Synthesis of (*o*-Hydroxyphenyl)acetylene (4). Compound **4** was prepared from benzofuran according to the procedure published by Prey.[11]

Synthesis of β,β-Dibromo-*o*-(trimethylsiloxy)styrene. Triphenylphosphine (48.0 mmol) was added to a stirring solution of carbon tetrabromide (24.0 mmol) in 120 mL of dry CH_2Cl_2 (under N_2) and cooled to 0 °C.[12] After 15 min, *o*-(trimethylsiloxy)benzaldehyde[13] (20.0 mmol) was added rapidly, and the mixture was stirred for 7 min. The orange solution was slowly poured into 1.8 L of stirring hexane, solids were allowed to coagulate, and the clear solution was decanted. Solvents down to ca. 50 mL were removed by using a rotary evaporator, followed by removal of triphenylphosphine oxide by filtration. The filtrate was added to 500 mL of recovered hexane causing the precipitation of additional triphenylphosphine oxide which was again removed by filtration. After removal of the bulk of the hexane using a rotary evaporator, residual solvent was removed under high vacuum (0.1 torr), leaving nearly pure β,β-dibromo-*o*-(trimethylsiloxy)styrene as a greenish yellow oil (6.34 g, 18.1 mmol): ^{1}H NMR δ 0.30 (s, 9 H), 6.75–7.85 (m, 5 H); ^{13}C NMR δ 0.35, 89.74, 115.90, 119.75, 121.27, 129.23, 129.77, 133.83, 134.21; IR 3070, 3030, 2960, 1600, 1570, 1480, 1450, 1280, 1265, 1250, 1100, 915, 870, 840, 770, 750, 690 cm^{-1}; MS, m/e (relative intensity) 352 (17) (M + 4), 350 (32) (M + 2), 348 (16) (M$^+$), 139 (90), 137 (90), 73 (100); calcd for $C_{11}H_{14}Br_2OSi$ m/e 347.91806, measured m/e 347.91742. Attempts to further purify the product by distillation or chromatography resulted in decomposition.

Synthesis of *o*-[(Trimethylsilyl)ethynyl]phenol (7). A solution of β,β-dibromo-*o*-(trimethylsilyl)styrene (2.86 mmol) in dry THF (20 mL) was cooled to −78 °C. A solution of *n*-butyllithium in hexane (7.4 mmol, 2.3 M) was then added dropwise. After complete addition, the dark green solution was stirred for 1 h at −78 °C, warmed to room temperature, and stirred 4 h longer. The solution was added to water saturated with NH_4Cl and extracted with three 25-mL portions of Et_2O. The organic portion was then washed with H_2O and dried over $MgSO_4$. After filtration and removal of solvent, the residual oil was purified by column chromatography on a silica gel column eluted with 1:9 hexane/ethyl acetate. A solid was isolated which after sublimation (0.1 torr, 50 °C) gave pure **7**, 0.41 g (75%): mp 46–47 °C; ^{1}H NMR δ 0.26 (s, 9 H), 5.98 (s, 1 H), 6.58–7.41 (m, 4 H); ^{13}C NMR δ −0.026, 99.00, 109.51, 114.55, 120.18, 130.64, 131.61, 131.88, 157.13; IR (KBr pellet) 3250, 2960, 2870, 2150, 1600, 1480, 1450, 1290, 1245, 1060, 865, 840, 750 cm^{-1}; MS, m/e (relative intensity) 190 (22), 175 (100), 159 (18), 135 (13), 115 (17); calcd for $C_{11}H_{14}OSi$ m/e 190.08140, measured m/e 190.08139. Anal. Calcd for $C_{11}H_{14}$: C, 69.42; H, 7.41. Found: C, 69.28; H, 7.50. This reaction gave poor yields (5–25%) in subsequent attempts.

Synthesis of 3-(Trimethylsilyl)benzofuran (9). 3-Bromobenzofuran (7.42 mmol), prepared by the method of Stoermer and Kahlert,[14] was dissolved in 35 mL of Et_2O and cooled to −115 °C. A solution of *n*-butyllithium in hexane (7.43 mmol, 2.5 M) was slowly added dropwise followed by stirring at −115 °C for 1 h. Trimethylchlorosilane (8.9 mmol) was then added dropwise, keeping the reaction temperature below −100 °C at all times. The mixture was slowly warmed to room temperature over a 3-h period and then extracted with additional Et_2O and aqueous NaCl. After drying with $MgSO_4$, followed by removal of the drying agent and solvent, the residue was chromatographed on silica gel eluted with hexane/ethyl acetate (9:1). A 31% yield (2.31 mmol) of **7** was obtained. In addition, 0.84 mmol (11%) of 3-(trimethylsilyl)benzofuran (**9**) was isolated from a second chromatographed sample after preparative GC on a 10 ft × 0.25 in. 15% SE-30 Chromosorb W column at 200 °C: ^{1}H NMR δ 0.35 (s, 9 H), 7.15–7.71 (m, 5 H), included within the multiplet was a singlet at δ 7.47 which was assigned to the vinyl hydrogen adjacent to silicon on the furan ring; ^{13}C NMR δ −0.72, 111.36, 120.15, 121.99, 122.49, 124.03, 131.22, 149.56, 155.87; IR 3070, 2970, 1520, 1450, 1265, 1255, 1110, 1080, 1005, 835, 765, 745 cm^{-1}; MS m/e (relative intensity) 190 (23), 176 (19), 175 (100), 145 (5), 135 (5), 115 (6), 101 (4), 87 (9); calcd for $C_{11}H_{14}OSi$ m/e 190.08140, measured m/e 190.08079. Anal. Calcd for $C_{11}H_{14}$: C, 69.42; H, 7.41. Found: C, 69.14; H, 7.24. A small amount (10%) of [*o*-(trimethylsiloxy)(trimethylsilyl)phenyl]acetylene was also obtained after preparative GC of the mixture obtained after column chromatography: ^{1}H NMR δ 0.24 (s, 9 H), 0.28 (s, 9 H), 6.75–7.50 (m, 4 H); IR 3080, 3040, 2970, 2920, 2170, 1600, 1570, 1490, 1450, 1390, 1255, 1105, 920, 870, 840, 760 cm^{-1}; MS, m/e (relative intensity) 262 (51), 248 (17), 247 (68), 231 (21), 207 (16), 193 (15), 73 (100); calcd for $C_{14}H_{22}OSi_2$ m/e 262.12093, measured m/e 262.12069. The procedure for lithium–bromine exchange used here was the same as that described by Cugnon de Sevricourt and Robba[15] who obtained 3-benzofurancarboxylic acid in 62%.

Synthesis of [*o*-(Trimethylsiloxy)phenyl]acetylene (10). The synthesis of **10** began with the synthesis of benzofuran[16] which was then converted to (*o*-hydroxyphenyl)acetylene[11] followed by protection of the hydroxyl group as the trimethylsilyl ether.[17]

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Synthesis of 2-(Trimethylsilyl)benzofuran (11). This compound was synthesized according to the procedure of Eaborn.[18]

Synthesis of 4,5-Dihydro-2-(trimethylsilyl)furan (15). Compound **15** was prepared from 4,5-dihydrofuran (Aldrich Chemical Co.) according to a procedure published by Erchak et al.[19]

Synthesis of β,β-Dibromo-o-methoxystyrene. Triphenylphosphine (76.98 mmol) was added to a stirring solution of carbon tetrabromide (38.49 mmol) in 100 mL of dry CH_2Cl_2 under N_2 cooled to 0 °C.[12] After 15 min, *o*-anisaldehyde (38.49 mmol) was added rapidly. The reaction was complete in 15 min and was slowly poured into 1.5 L of stirring hexane. The supernatant liquid was decanted, and solvent was removed by using a rotary evaporator. The triphenylphosphine oxide was removed by filtration and washed with additional hexane. Solvent was removed from the filtrate, and the oil was chromatographed on silica gel eluted with hexane/ethyl acetate (9:1). After removal of solvent, the title compound (34.56 mmol, 90% yield) was obtained as a light yellow crystalline solid with mp 31–33 °C: ^{1}H NMR δ 3.8 (s, 3 H), 6.7–7.8 (m, 5 H); ^{13}C NMR δ 55.5, 89.63, 101.55, 110.54, 120.18, 129.12, 129.93, 132.91, 156.59; IR 3040, 3020, 2980, 2950, 2850, 1600, 1580, 1485, 1465, 1440, 1290, 1250, 1110, 1050, 1025, 870, 810, 740 cm^{-1}; MS, *m/e* (relative intensity) 294 (28) (M + 4), 292 (55) (M + 2), 290 (29) (M^+), 213 (35), 211 (36), 198 (55), 196 (57), 185 (16), 183 (16), 132 (85), 131 (100), 104 (32), 102 (22), 89 (96), 63 (44); calcd for $C_9H_8OBr_2$ *m/e* 289.89418, measured *m/e* 289.89452.

Synthesis of (o-Methoxyphenyl)acetylene (23). A solution of β,β-dibromo-*o*-methoxystyrene (14.94 mmol) in dry THF (90 mL) under N_2 was cooled to −78 °C. A solution of *n*-butyllithium in hexane (31.4 mmol, 2.1 M) was then added dropwise resulting in a deep red solution which was stirred for 1 h at −78 °C and 1 h at room temperature. Excess H_2O was then added, and the mixture was extracted with 75 mL of Et_2O, washed with more H_2O, and dried with $MgSO_4$. After removal of the drying agent and solvent, the residual oil was distilled (80–82 °C, 1 torr) to give **23** (10.76 mmol, 72%): ^{1}H NMR δ 3.3 (s, 1 H), 3.9 (s, 3 H), 6.8–7.6 (M, 4 H); MS, *m/e* (relative intensity) 132 (100), 131 (91), 89 (37), 77 (12), 63 (27), 62 (12), 51 (11); GCIR 3330, 3080, 3010, 2950, 2840, 2110, 1610, 1490, 1440, 1260, 1215, 1110, 1040 cm^{-1}.

Synthesis of 2-Methylbenzofuran (26). The procedure of Baciocchi et al.[20] was used to prepare 2-methylbenzofuran from benzofuran.

Synthesis of 1,2-Benzopyran (25). Compound **25** was prepared according to the procedure described by Iwai and Ide[21] by the sequence phenol → phenyl propargyl ether → 1,2-benzopyran.

Synthesis of (o-Methoxyphenyl)-1-propyne (27). A solution of β,β-dibromo-*o*-methoxystyrene (22.8 mmol) in dry THF (140 mL) under N_2 was cooled to −78 °C. A solution of *n*-butyllithium in hexane (47.9 mmol, 2.4 M) was then added dropwise, resulting in a deep red solution which was stirred for 1 h at −78 °C and 1 h at room temperature. Dimethyl sulfate (27.3 mmol) was added dropwise followed by stirring for 2 h. The reaction mixture was poured into 100 mL of H_2O and extracted with pentane. The organic layer was washed with several portions of H_2O and dried with $MgSO_4$. The drying agent was removed by gravity filtration, and solvent was removed on a rotary evaporator. The residual oil was distilled (115–117 °C, 9 torr) to yield **27** (16.76 mmol, 74%): ^{1}H NMR δ 2.11 (s, 3 H), 3.87 (s, 3 H), 6.80–6.95 (m, 2 H), 7.23 (d of t, 1 H, *J* = 7.8 and 1.6 Hz), 7.37 (d of d, 1 H, *J* = 7.5 and 1.6 Hz).

Synthesis of (o-Methoxyphenyl)(trimethylsilyl)acetylene (31). A solution of β,β-dibromo-*o*-methoxystyrene (18.68 mmol) in dry THF (110 mL) under N_2 was cooled to −78 °C. A solution of *n*-butyllithium in hexane (39.22 mmol, 2.3 M) was then added dropwise which resulted in a deep red solution that was stirred for 1 h at −78 °C and 1 h at room temperature. Trimethylchlorosilane (22.4 mmol) was then added rapidly, and the mixture was stirred for an additional 1 h. The product was extracted with 100 mL of Et_2O, washed with three 75-mL portions of H_2O, and dried with $MgSO_4$. After removal of the drying agent and solvent, the residual oil was distilled (72–74 °C, 0.2 torr), yielding **31** (14.38 mmol, 77%): ^{1}H NMR δ 0.3 (s, 9 H), 3.8 (s, 3 H), 6.7–7.5 (m, 4 H); ^{13}C NMR δ 0.08, 55.72, 98.30, 101.37, 110.76, 112.38, 120.29, 129.93, 134.11, 160.33; IR 3072, 3005, 2959, 2899, 2835, 2158, 1595, 1576, 1491, 1464, 1435, 1292, 1281, 1258, 1115, 1047, 1026, 866, 843, 752 cm^{-1}; MS, *m/e* (relative intensity) 204 (52), 189 (100), 161 (38), 159 (35), 135 (8), 115 (45), 95 (17); calcd for $C_{12}H_{16}OSi$ *m/e* 204.09705, measured *m/e* 204.0952. Anal. Calcd for $C_{12}H_{16}$: C, 70.53; H, 7.89. Found: C, 70.46; H, 8.10.

Synthesis of 2-Ethylbenzofuran (28). The preparation of compound **28** was carried out by the sequence salicaldehyde → 2-acetylbenzofuran → 2-ethylbenzofuran according to published procedures.[22]

Synthesis of (Trimethylsilyl)phenylacetylene (32). Compound **32** was prepared from phenylacetylene as described by Eaborn and Walton.[23]

Synthesis of 2-Methyl-3-(trimethylsilyl)furan (34). Compound **34** was prepared by using the procedure of Sato and Katsuno[24] from (trimethylsilyl)propargyl alcohol and acetonitrile. The product was purified by preparative GC on a 9 ft × 0.25 in. 20% SE-30 Chromosorb W column temperature programmed from 100 to 250 °C at 5 °C per min to give **34** in 28% yield: ^{1}H NMR δ 0.24 (s, 9 H), 2.35 (s, 3 H), 6.27 (d, 1 H, *J* = 1.6 Hz), 7.32 (d, 1 H, *J* = 1.6 Hz); ^{13}C NMR δ −0.42, 14.33, 112.04, 114.62, 140.19, 156.72; IR 2970, 1570, 1510, 1385, 1250, 1215, 1025, 890, 835, 755, 725 cm^{-1}; MS, *m/e* (relative intensity) 154 (27), 139 (100), 111 (28), 109 (14), 99 (12), 83 (12), 73 (26), 69 (14), 65 (8), 61 (21), 59 (10), 53 (8); calcd for $C_8H_{14}OSi$ *m/e* 154.08140, measured *m/e* 154.08109. Anal. Calcd for C_8H_{14}: C, 62.28; H, 9.15. Found: C, 62.07; H, 9.20.

Synthesis of *cis*-1-(Trimethylsilyl)-4-methoxy-3-buten-1-yne (35). Compound **35** was prepared from *cis*-4-methoxy-3-buten-1-yne (**40**) (Aldrich Chemical Co.) after purification by extraction with H_2O and Et_2O, drying of the Et_2O layer with Na_2SO_4, and distillation (bp 122–125 °C). A solution of *n*-butyllithium in hexane (45.0 mmol, 2.4 M) was added dropwise to **40** (44.4 mmol) in 110 mL of THF cooled to 0 °C. After 20 min, trimethylchlorosilane (46.0 mmol) was rapidly added and stirred for 1 h. The mixture was poured into H_2O, extracted with pentane, and dried with $MgSO_4$. Solvent was removed by distillation at ambient pressure. The residual yellow liquid was distilled (25 °C, 0.1 torr) into a flask cooled to −78 °C. The product (32.4 mmol, 73%), which yellowed rapidly upon standing, could be further purified by preparative GC on a 9 ft × 0.25 in. 20% SE-30 Chromosorb W column at 125 °C: ^{1}H NMR δ 0.17 (s, 9 H), 3.76 (s, 3 H), 4.54 (d, 1 H, *J* = 6.5 Hz), 6.24 (d, 1 H, *J* = 6.5 Hz); ^{13}C NMR δ 0.07, 60.63, 85.33, 97.62, 99.47, 157.09; IR 2970, 2140, 1635, 1455, 1385, 1270, 1250, 1110, 950, 840, 755, 725, 690 cm^{-1}; MS, *m/e* (relative intensity) 154 (26), 139 (100), 109 (33), 83 (11), 69 (9), 59 (16); calcd for $C_8H_{14}OSi$ *m/e* 154.08140, measured *m/e* 154.08123. Anal. Calcd for C_8H_{14}: C, 62.28; H, 9.15. Found: C, 62.35; H, 9.39.

Synthesis of [o-(Trimethylsiloxy)phenyl]-1-propyne (42). The preparation of **42** was accomplished from 3-bromo-2-methylbenzofuran synthesized by the following sequence: benzofuran → 2-methylbenzofuran[20] → 2,3-dibromo-2-methylbenzofuran → 3-bromo-2-methylbenzofuran → 3-lithio-2-methylbenzofuran.[25] The 3-lithio-2-methylbenzofuran was prepared from 3-bromo-2-methylbenzofuran (12.33 mmol) in Et_2O (60 mL) at −78 °C by the slow addition of a solution of *n*-butyllithium in hexane (13.57 mmol, 2.4 M). After being stirred for 20 min at −78 °C, the solution was slowly warmed to room temperature (2 h) and stirred an addition 2 h. Trimethylchlorosilane (14.79 mmol) was added rapidly and stirred for 12 h. Salts were removed by filtration and solvent was distilled off at ambient pressure. The residue was distilled (50 °C, 0.1 torr) into a trap

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cooled to −78 °C. This clear distillate was redistilled (93–97 °C, 4 torr) to give **42** (2.12 mmol, 84%): ^{1}H NMR δ 0.28 (s, 9 H), 2.07 (s, 3 H), 6.80 (d, 1 H, J = 8.1 Hz), 6.89 (t, 1 H, J = 7.5 Hz), 7.14 (d of t, 1 H, J = 8.2 and 1.3 Hz), 7.33 (unresolved d of d, 1 H, J = 7.7 Hz); ^{13}C NMR δ 0.39 (t, J = 29 Hz), 4.42, 89.29, 114.91, 116.79, 120.24, 121.41, 128.63, 133.18, 156.33; IR 3071, 3032, 2959, 2916, 2233, 1597, 1568, 1489, 1445, 1283, 1264, 1254, 1107, 916, 845, 766, 741 cm^{-1}; m/e (relative intensity) 204 (39), 189 (61), 161 (33), 115 (100); calcd for $C_{12}H_{16}OSi$ m/e 204.09705, measured m/e 204.09728. Anal. Calcd for $C_{12}H_{16}$: C, 70.53; H, 7.89. Found: C, 70.74; H, 8.07.

FVP of (*o*-Hydroxyphenyl)acetylene (4). (i) Compound **4** (73 mg), distilled (1 × 10^{-2} torr) from a bath at 0 °C, was pyrolyzed at 750 °C. Analysis of the pyrolysate (52 mg, 71%) by ^{1}H NMR and GC revealed benzofuran (**6**) (71%, GC yield) as the sole product. Identification was made by comparison of ^{1}H NMR, IR, and GCMS data with that from an authentic sample.

(ii) Compound **4** (53 mg) was pyrolyzed at 650 °C (1 × 10^{-2} torr). Analysis of the pyrolysate (39 mg, 74%) by ^{1}H NMR revealed benzofuran (**6**) and starting material in a ratio of 93:7.

(iii) Compound **4** (67 mg) was pyrolyzed at 540 °C (1 × 10^{-2} torr.) Analysis of the pyrolysate (62 mg, 93%) by ^{1}H NMR and GC revealed **6** and **4** present in a ratio of 71:29 (determined by GC).

FVP of (*o*-Hydroxyphenyl)(trimethylsilyl)acetylene (7). (i) Compound **7** (41 mg) was pyrolyzed at 480 °C (10^{-2} torr). A sample of the pyrolysate (34 mg, 83%) was analyzed by ^{1}H NMR and found to contain starting material **7**, [*o*-(trimethylsiloxy)-phenyl]acetylene (**10**), and 3-(trimethylsilyl)benzofuran (**9**) in ratios of 84.9:11.9:3.1. Identification of the products was made, after isolation by preparative GC (10 ft × 0.25 in. 15% SE-30 on Chromosorb W at 185 °C), by comparison of ^{1}H NMR, ^{13}C NMR, IR, and GCMS spectra with synthetic samples.

(ii) Compound **7** (53 mg) was pyrolyzed at 540 °C (10^{-2} torr). A sample of the pyrolysate (50 mg, 94%) was analyzed by ^{1}H NMR and found to contain **7**, **10**, and **9** in ratios of 40.8:40.8:18.4.

(iii) Compound **7** (41 mg) was pyrolyzed at 650 °C (10^{-2} torr). A sample of the pyrolysate (32 mg, 78%) was analyzed by ^{1}H NMR and found to contain **10**, 2-(trimethylsilyl)benzofuran (**11**), and **9** in ratios of 50.1:18.8:31.1. Compound **11** was identified as a mixture with the 3-isomer **9**, after preparative GC (10 ft × 0.25 in. 15% SE-30 on Chromosorb W at 185 °C), by comparison of the ^{1}H NMR, ^{13}C NMR, IR, and GCMS with a synthetic sample of **11**.

(iv) Compound **7** (41 mg) was pyrolyzed at 700 °C (10^{-2} torr). A sample of the pyrolysate (30 mg, 73%) was analyzed by ^{1}H NMR and found to contain **10**, **11**, and **9** in ratios of 37.4:27.6:35.0.

(v) Compound **7** (56 mg) was pyrolyzed at 750 °C (10^{-2} torr). A sample of the pyrolysate (51 mg, 91%) was analyzed by ^{1}H NMR and found to contain **10**, **11**, and **9** in ratios of 34.4:29.7:35.9.

(vi) Compound **7** (29 mg) was pyrolyzed at 800 °C (10^{-2} torr). The pyrolysate was collected (22 mg, 76%) and a sample analyzed by ^{1}H NMR revealed **10**, **11**, and **9** in ratios of 36.7:28.4:34.9.

(vii) Compound **7** (80 mg) was pyrolyzed at 700 °C at 1 × 10^{-5} torr instead of 1 × 10^{-2} torr. The pyrolysate was collected (74 mg, 92%), and a sample was analyzed by ^{1}H NMR. Compounds **10**, **11**, and **9** were found to be present in ratios of 43.4:20.3:36.3.

FVP of 3-(Trimethylsilyl)benzofuran (9). (i) Compound **9** (38 mg, distilled 1 × 10^{-2} torr), from a bath at 40 °C, was pyrolyzed at 700 °C. The pyrolysate was collected (36 mg, 96%) and analyzed by ^{1}H NMR. Only starting material was present.

(ii) Compound **9** (40 mg) was pyrolyzed at 800 °C (1 × 10^{-2} torr). Analysis of the pyrolysis (33 mg, 82%) by ^{1}H NMR revealed [*o*-(trimethylsiloxy)phenyl]acetylene (**10**), 2-(trimethylsilyl)-benzofuran (**11**), and starting material in ratios of 20.7:10.4:68.9. Products were further characterized, after separation of **10** from **9** and **11** by preparative GC (10 ft × 0.25 in. 15% SE-30 on Chromosorb W at 185 °C), by comparison of ^{1}H NMR, IR, and GCMS with authentic samples.

FVP of [*o*-(Trimethylsiloxy)phenyl]acetylene (10). (i) Compound **10** (45 mg), distilled (1 × 10^{-2} torr) from a bath at 40 °C, was pyrolyzed at 540 °C. The pyrolysate (43 mg, 96%), analyzed by ^{1}H NMR, consisted only of starting material.

(ii) Compound **10** (57 mg) was pyrolyzed at 700 °C (1 × 10^{-2} torr). Analysis of the pyrolysate (55 mg, 96%) by ^{1}H NMR revealed 2-(trimethylsilyl)benzofuran (**11**) and starting material in ratios of 39.4:60.6. Product identification was confirmed, after separation by preparative GC (10 ft × 0.25 in. 15% SE-30 on Chromosorb W at 185 °C), by comparison of ^{1}H NMR, IR, and GCMS with authentic samples.

(iii) Compound **10** (53 mg) was pyrolyzed at 750 °C (1 × 10^{-2} torr). Analysis of the pyrolysate (50 mg, 94%) by ^{1}H NMR revealed 3-(trimethylsilyl)benzofuran (**9**), 2-(trimethylsilyl)-benzofuran (**11**), and starting material in ratios of 11.8:38.4:49.8. The presence of **9** was confirmed, after separation from **10** by preparative GC (10 ft × 0.25 in. 15% SE-30 on Chromosorb W at 185 °C), by comparison of ^{1}H and ^{13}C NMR spectra with those from an authentic sample.

(iv) Compound **10** (63 mg) was pyrolyzed at 800 °C (1 × 10^{-2} torr). Analysis of the pyrolysate (57 mg, 88%) by ^{1}H NMR revealed 3-(trimethylsilyl)benzofuran (**9**), 2-(trimethylsilyl)-benzofuran (**11**), and starting material in ratios of 31.2:20.2:48.6.

FVP of 2-(Trimethylsilyl)benzofuran (11). (i) Compound **11** (216 mg), distilled (1 × 10^{-2} torr) from a bath at 40 °C, was pyrolyzed at 700 °C. Analysis of the pyrolysate (202 mg, 93.5%) by ^{1}H NMR revealed [*o*-(trimethylsiloxy)phenyl]acetylene (**10**) and starting material in a ratio of 64.9:35.1. Identification of **10** and **11** was made, after separation by preparative GC (10 ft × 0.25 in. 15% SE-30 on Chromosorb W at 185 °C), by comparison of ^{1}H NMR, IR, and GCMS data with that obtained from authentic samples.

(ii) Compound **11** (43 mg) was pyrolyzed at 750 °C (1 × 10^{-2} torr). Analysis of the pyrolysate (39 mg, 91%) by ^{1}H NMR revealed [*o*-(trimethylsiloxy)phenyl]acetylene (**10**), 3-(trimethylsilyl)benzofuran (**9**), and starting material in ratios of 46.7:8.6:44.7.

(iii) Compound **11** (50 mg) was pyrolyzed at 800 °C (1 × 10^{-2} torr). Analysis of the pyrolysate (42 mg, 84%) by ^{1}H NMR revealed compounds **9**, **10**, and **11** in ratios of 21.9:45.1:32.9. Product identification was confirmed, after separation of **10** from **9** and **11** by preparative GC (10 ft × 0.25 in. 15% SE-30 on Chromosorb W at 185 °C) and by comparison of ^{1}H and ^{13}C NMR, IR, and GCMS data with spectra obtained from authentic samples.

FVP of 4,5-Dihydro-2-(trimethylsilyl)furan (15). (i) Compound **15** (224.6 mg), distilled (1 × 10^{-4} torr) from a bath warmed slowly from −10 to 0 °C was pyrolyzed at 650 °C. The pyrolysate was collected (198.1 mg, 88.2%), and the products were separated by preparative GC (9 ft × 0.25 in. 15% SE-30 on Chromosorb W temperature programmed from 80 to 250 °C at 3 °C per min). From the pyrolysate, 4-(trimethylsiloxy)-1-butyne (**17**), (trimethylsilyl)ketene (**20**), and 2-(trimethylsiloxy)-1,3-butadiene (**22**) were obtained in 49%, 33%, and 5% yield (by GC), respectively. Compound **17** was identified by comparison of its spectra with an authentic sample: ^{1}H NMR δ 0.12 (s, 9 H), 1.96 (t, 1 H, J = 2.6 Hz), 2.40 (d of t, 2 H, J = 7.1 and 2.6 Hz), 3.70 (t, 2 H, J = 7.1 Hz); IR 3320, 2965, 2930, 2890, 2130, 1390, 1255, 1100, 1060, 915, 870, 840, 750 cm^{-1}; GCMS, m/e (relative intensity) 127 (47), 109 (14), 103 (75), 97 (62), 75 (13), 73 (100). **20**: ^{1}H NMR δ 0.17 (s, 9 H), 1.79 (s, 1 H); ^{13}C NMR δ −0.06, 0.68, 179.51; IR 3370, 3050, 2970, 2910, 2115, 1270, 1250, 1050, 840 cm^{-1}; GCMS, m/e (relative intensity) 114 (21), 99 (100), 73 (7), 69 (7), 55 (7). Spectra obtained for **20** matched published spectra.[6,26,27] **22**: ^{1}H NMR δ 0.24 (s, 9 H), 4.35 (s, 1 H), 4.36 (s, 1 H), 5.09 (d of t, 1 H, J = 10.4 and 1.6 Hz), 5.47 (d of d, 1 H, J = 17.0 and 1.8 Hz), 6.20 (d of d, 1 H, J = 17.0 and 10.4 Hz); ^{13}C NMR δ 0.07, 96.45, 114.57, 134.67, 154.92; IR 3130, 3110, 3030, 2980, 2920, 1640, 1595, 1410, 1380, 1260, 1060, 1010, 985, 920, 880, 845, 750 cm^{-1}; GCMS, m/e (relative intensity) 142 (25), 127 (77), 111 (5), 99 (7), 85 (53), 75 (100), 73 (33), 61 (11), 59 (12). The ^{1}H NMR was consistent with that reported in the literature.[28]

(ii) Compound **15** (174.6 mg) was also pyrolyzed at 600 °C (4 × 10^{-5} torr). The pyrolysate was collected (164.6 mg, 94.3%) and analyzed by GC and NMR. Compounds **17**, **20**, and **22** were determined (by GC) to be present in 54%, 34%, and 5% yield, respectively, based on 13% recovered starting material.

FVP of 4,5-Dihydrofuran. A sample of 4,5-dihydrofuran

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(334.56 mg), distilled (2×10^{-5} torr) from a bath warmed slowly from −30 to 0 °C, was pyrolyzed at 700 °C. The pyrolysate was collected (272.8 mg, 81.6%) and products were isolated by preparative GC on a 9 ft × 0.25 in. 15% SE-30 Chromosorb W column temperature programmed from 80–250 °C at 6 °C per min. The products were identified by comparison of ^{1}H NMR and GCMS with authentic samples as cyclopropanecarboxaldehyde and *cis*- and *trans*-crotonaldehyde in a 1:1 ratio in 39% and 26% yield based on 44% recovered starting material. The flow pyrolysis of 4,5-dihydrofuran has already been reported and gave the same products.[7]

FVP of (*o*-Methoxyphenyl)acetylene (23). Compound **23** (131.0 mg), distilled (2×10^{-5} torr) from a bath at 50 °C, was pyrolyzed at 700 °C. The pyrolysate was collected (90.0 mg, 68.7%), and the products were isolated by preparative GC on a 10 ft × 0.25 in. 15% SE-30 Chromosorb W Column temperature programmed from 100 to 250 °C at 6 °C per min. The isolated products, phenylacetylene (1%), styrene (5%), benzofuran (**6**) (23%), and 2-methylbenzofuran (**26**) (7%), were identified by comparison of GCMS and ^{1}H NMR spectra with authentic material. Yields were determined by GC analysis and based on 14% recovered starting material.

FVP of 1,2-Benzopyran (25). Compound **25** (201.2 mg), distilled (2×10^{-5} torr) from a bath, heated slowly from 25 to 50 °C over a 40-min period, was pyrolyzed at 700 °C. Analysis of the pyrolysate (187.4 mg, 93.1%) by ^{1}H NMR and GC showed **25** unreacted (77%, by GC) and eight minor products present in low yield, but no 2-methylbenzofuran (**26**) or benzofuran (**6**).

FVP of 2-Methylbenzofuran (26). Compound **26** (114.9 mg) was pyrolyzed under the same conditions as **23** at 700 °C (2×10^{-5} torr). Only starting material was recovered (110.1 mg, 95.8%).

FVP of (*o*-Methoxyphenyl)-1-propyne (27). Acetylene **27** (117.7 mg), distilled (2×10^{-5} torr) at room temperature, was pyrolyzed at 700 °C. The pyrolysate (85.3 mg, 72.5%) was analyzed by GC and found to contain five products which were isolated by preparative GC on a 9 ft × 0.25 in. 15% SE-30 Chromosorb W column temperature programmed from 100 to 250 °C at a rate of 6 °C per min. The products were identified as 2-methylbenzofuran (**26**) (29%), 2-ethylbenzofuran (**28**) (15%), and a mixture of *o*-, *m*-, or *p*-methylstyrenes (9%) in approximately equal amounts. The yields were determined by GC analysis and based on 9% recovered starting material. Products were identified by comparison of the ^{1}H NMR and GCMS spectra with authentic materials.

FVP of 2-Ethylbenzofuran (28). Pyrolysis of **28** (306.1 mg), distilled (2×10^{-5} torr) from a bath slowly heated from 25 to 60 °C, was pyrolyzed at 700 °C. The pyrolysate contained only 2-ethylbenzofuran (297.3 mg, 97.1%). However, pyrolysis of **28** (337.9 mg) at 800 °C (2×10^{-5} torr) gave a pyrolysate (321.5 mg, 95.1%) containing **28** (80%), 2-methylbenzofuran (**26**) (25%), and benzofuran (**6**) (10%). Yields were determined by GC analysis and are corrected for recovered **28**. The products were identified by comparative GCMS and ^{1}H NMR with authentic samples. Isolation of individual components was achieved by preparative GC on a 9 ft × 0.25 in. 15% SE-30 Chromosorb W column temperature programmed from 100 to 250 °C at a rate of 6 °C per min.

FVP of (*o*-Methoxyphenyl)(trimethylsilyl)acetylene (31). (i) Compound **31** (131.2 mg), distilled (1×10^{-4} torr) from a bath heated from 80 to 120 °C over a 1-h period, was pyrolyzed at 750 °C. Only one major product was present and was isolated by preparative GC on a 9 ft × 0.25 in. 10% SE-30 Chromosorb W column temperature programmed from 180 to 250 °C at 5 °C per min. The product was determined to be 2-ethylbenzofuran (**28**) (45%, by GC) by comparison of GCMS, ^{1}H NMR, and ^{13}C NMR data with that from an authentic sample. Starting material (1%) was also recovered.

(ii) Pyrolysis of **31** (135.2 mg) at 700 °C (1×10^{-4} torr) gave a pyrolysate (100.9 mg, 74.6%) primarily consisting of 2-ethylbenzofuran (**28**) (42%, by GC) based on recovered starting material (12%).

(iii) Compound **31** (126.5 mg) was also pyrolyzed at 650 °C (1×10^{-4} torr). The pyrolysate (101.2 mg, 80.0%) contained **28** (32%, by GC) based on 38% recovered **31**.

(iv) Pyrolysis of **31** (125.3 mg) at 600 °C (1×10^{-5} torr) gave only recovered starting material (115.0 mg, 91.8%).

FVP of (Trimethylsilyl)phenylacetylene (32). Acetylene **32** (361.3 mg), distilled (1×10^{-3} torr) from a bath warmed slowly from 25 to 60 °C, was pyrolyzed at 900 °C. The pyrolysate (253.4 mg, 70.1%) contained several products which were separated and isolated by preparative GC on a 5 ft × 0.25 in. 20% SE-30 Chromosorb W column temperature programmed from 120 to 250 °C at a rate of 6 °C per min. Identified by comparative GCMS and ^{1}H NMR were phenylacetylene (17%), indene (4%), and 1-phenylpropyne (2%). Yields were determined by GC analysis and were based on recovered starting material (47%).

FVP of 2-Methyl-3-(trimethylsilyl)furan (34). Compound **34** (128.1 mg), distilled (1×10^{-5} torr) from a bath at 0 °C, was pyrolyzed at 650 °C. The pyrolysate (125.2 mg, 97.7%) contained only **34**. Pyrolysis of **34** (180.5 mg) at 800 °C (1×10^{-3} torr) produced four products in addition to starting material. These products were isolated by preparative GC on a 9 ft × 0.25 in. 20% SE-30 Chromosorb W column temperature programmed from 100 to 250 °C at 3 °C per min. The products were identified as 1-(trimethylsilyl)-1,2-butadiene (**36**) (9%), 1-(trimethylsilyl)-1-butyne (5%), *cis*-1-(trimethylsiloxy)-1-penten-3-yne (*cis*-**37**) (15%), and *trans*-1-(trimethylsiloxy)-1-penten-3-yne (*trans*-**37**) (15%). Yields were determined by GC analysis and based on 45% recovered starting material. Compounds *cis*-**37** and *trans*-**37** were identified by comparison of ^{1}H NMR and GCMS data obtained from the FVP of **35**. 1-(Trimethylsilyl)-1-butyne: ^{1}H NMR δ 0.14 (s, 9 H), 1.14 (t, 3 H, J = 7.5 Hz), 2.23 (q, 2 H, J = 7.5 Hz); GCMS 126 (11), 111 (100), 109 (14), 83 (24), 78 (14), 59 (11), 55 (10), 53 (9). *trans*-**37**: ^{1}H NMR δ 0.19, (s, 9 H), 1.90 (d, 3 H, J = 2.3 Hz), 5.11 (d of q, 1 H, J = 12.0 and 2.3 Hz), 6.72 (d, 1 H, J = 12.0 Hz); ^{13}C NMR δ −0.47, 4.34, 75.42, 84.26, 92.91, 150.77; IR 3050, 2970, 2930, 2870, 2210, 1640, 1270, 1260, 1210, 1150, 885, 845, 750 cm^{-1}; MS, m/e (relative intensity) 154 (42), 139 (45), 111 (23), 109 (11), 99 (9), 83 (9), 75 (8), 73 (100), 61 (19), 53 (9); calcd for $C_8H_{14}OSi$ m/e 154.08140, measured m/e 154.08137. Satisfactory elemental analysis could not be obtained for this compound.

FVP of *cis*-1-(Trimethylsilyl)-4-methoxy-3-buten-1-yne (35). Enyne **35** (304.8 mg), distilled (8×10^{-4} torr) from a bath warmed slowly from 25 to 40 °C, was pyrolyzed at 650 °C. The pyrolysate was collected (175.5 mg, 57.6%), and the products were isolated by preparative GC using a 9 ft × 0.25 in. 15% SE-30 Chromosorb W column temperature programmed from 100 to 250 °C at a rate of 5 °C per min. Identified were 1-(trimethylsilyl)-1,2-butadiene (**36**) (30%) and *cis*-1-(trimethylsiloxy)-1-penten-3-yne (*cis* **37**) (7%) based on 16% recovered starting material. Identification of **36** and *cis*-**37** was based on their spectra. **36b**: ^{1}H NMR δ 0.08 (s, 9 H), 1.16 (d of d, J = 7.0 and 4.0 Hz), 4.72 (overlapped d of q, apparent pentet, 1 H, J = 7.0 and 7.0 Hz), 4.85 (m, 1 H); ^{13}C NMR δ −0.85, 13.25, 77.80, 82.30, 210.96; IR 2970, 2930, 2900, 2870, 1945, 1365, 1250, 1195, 840, 755, 695 cm^{-1}; GCMS, m/e (relative intensity) 126 (16), 111 (10), 83 (26), 73 (100). *cis*-**37**: ^{1}H NMR δ 0.24 (s, 9 H), 1.97 (poorly resolved d, 3 H, J = 2 Hz), 4.60 (d of d, 1 H, J = 2.3 and 6.0 Hz), 6.39 (d, 1 H, J = 6.0 Hz); ^{13}C NMR δ −0.30, 4.65, 74.11, 88.87, 90.90, 147.92; IR 3040, 2970, 2930, 2870, 2220, 1630, 1440, 1410, 1270, 1255, 1165, 1085, 1070, 905, 840, 745 cm^{-1}; MS 154 (34), 139 (37), 111 (20), 99 (9), 83 (9), 75 (9), 73 (100), 61 (17); calcd for $C_8H_{14}OSi$ m/e 154.08140, measured m/e 154.08094. Anal. Calcd for C_8H_{14}: C, 62.28; H, 9.15. Found: C, 62.24; H, 9.24.

FVP of *cis*-4-Methoxy-3-buten-1-yne (40). Compound **40** (410.0 mg), distilled (1×10^{-3} torr) from a bath at 0 °C, was pyrolyzed at 650 °C. The pyrolysate was collected at −196 °C, and a portion of the most volatile components were transferred, using standard vacuum transfer techniques, to an NMR tube containing $CDCl_3$. An additional sample was utilized for GCMS, and the remainder was transferred to a gas cell for IR analysis. Two major volatile components, 1-butyne and 1,2-butadiene, were identified spectroscopically. 1-Butyne: ^{1}H NMR δ 0.98 (t, 3 H, J = 7.0 Hz), 1.85 (t, 1 H, J = 2.7 Hz), 1.95 (d of q, 2 H, J = 7.0 and 2.7 Hz); GCMS, m/e (relative intensity) 54 (96), 53 (44), 52 (11), 51 (24), 50 (30), 49 (10), 39 (100), 38 (21), 37 (13); IR (gas phase) 3360, 3340, 2140 cm^{-1}. 1,2-Butadiene: ^{1}H NMR δ 1.56 (overlapped d of t, 3 H, J = 7.0 and 3.5 Hz), 4.65 (overlapped d of q, 2 H, J = 7.0 and 3.5 Hz), 5.05 (m, 1 H); GCMS, m/e (relative intensity) 54 (100), 53 (41), 52 (12), 51 (26), 50 (29), 49 (9), 39 (48),

38 (10), 37 (7); IR (gas phase) 1975 cm^{-1}. Although starting material was recovered, none was present in the volatile samples examined by IR and NMR. The NMR spectra of both isomers were consistent with published data,[29] as were the mass spectra.[30,31]

FVP of [*o*-(Trimethylsiloxy)phenyl]-1-propyne (42). (i) Compound **42** (150.4 mg), distilled (1×10^{-5} torr) from a bath heated from 60 to 80 °C over a 20-min period, was pyrolyzed at 700 °C. Only starting material was present in the pyrolysate (140.9 mg, 93.7%).

(ii) Pyrolysis of compound **42** (127.9 mg) at 800 °C (2×10^{-4} torr) produced ten minor products in addition to recovered starting material which accounted for approximately two-thirds of the total recovered pyrolysate (127.9 mg, 82.6%).

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Registry No. **4**, 5101-44-0; **6**, 271-89-6; **7**, 81787-62-4; **9**, 93782-14-0; **10**, 61547-39-5; **11**, 60981-57-9; **15**, 75213-96-6; **17**, 17869-75-9; **20**, 4071-85-6; **22**, 38053-91-7; **23**, 767-91-9; **25**, 254-04-6; **26**, 4265-25-2; **27**, 66021-98-5; **28**, 3131-63-3; **31**, 40230-91-9; **32**, 2170-06-1; **34**, 93782-16-2; **35**, 93782-17-3; **36**, 14583-74-5; *cis*-**37**, 93782-18-4; *trans*-**37**, 93782-21-9; **40**, 3685-19-6; **42**, 93782-20-8; PhC≡CH, 536-74-3; $Me_3SiC{\equiv}C{-}Et$, 62108-37-6; PhC≡CMe, 673-32-5; β,β-dibromo-*o*-(trimethylsiloxy)styrene, 93782-13-9; carbon tetrabromide, 558-13-4; *o*-(trimethylsiloxy)benzaldehyde, 1078-31-5; *n*-butyllithium, 109-72-8; 3-bromobenzofuran, 59214-70-9; [*o*-(trimethylsiloxy)(trimethylsilyl)phenyl]acetylene, 93782-15-1; β,β-dibromo-*o*-methoxystyrene, 90585-32-3; *o*-anisaldehyde, 135-02-4; (trimethylsilyl)propargyl alcohol, 5272-36-6; acetonitrile, 75-05-8; 3-bromo-2-metylbenzofuran, 58863-48-2; 3-lithio-2-methylbenzofuran, 93782-19-5; 4,5-dihydrofuran, 1191-99-7; cyclopropanecarboxaldehyde, 1489-69-6; *trans*-crotonaldehyde, 123-73-9; *o*-methylstyrene, 611-15-4; *m*-methylstyrene, 100-80-1; *p*-methylstyrene, 622-97-9; indene, 95-13-6; 1-butyne, 107-00-6; 1,2-butadiene, 590-19-2; *cis*-crotonaldehyde, 15798-64-8; trimethylchlorosilane, 75-77-4.

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Photochemistry of 4-Pyrimidinones: Isolation of Dewar Isomers

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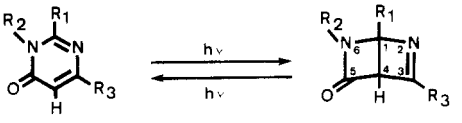
The 1,3,6-trialkyl-5-oxo-2,6-diazabicyclo[2.2.0]hex-2-enes (Dewar 4-pyrimidinones) **2a–d** which are formed in the photolysis of 2,3,6-trialkyl-4-pyrimidinones **1a–d** were isolated in yields of 16–24%. When 6-[(alkoxycarbonyl)methyl]-4-pyrimidinones **3a–c** were irradiated, 3-[(alkoxycarbonyl)methylene]-2,6-diazabicyclo[2.2.0]hexan-5-ones **4a–c** were formed. The *E* and *Z* isomers of **4** were isolated in total yields of 24–26%. The physical properties of the compounds were measured.

The photoisomerization of diazines and diazinones has been shown to result from transposition of ring nitrogen atoms and has been explained in terms of the valence-bond isomers.[1] However, very few valence-bond isomers of diazines and diazinones have been isolated.[2-4] Recently,[5c-e] spectroscopic evidence (IR, ^1H and ^{13}C NMR) was reported for the formation of the Dewar 4-pyrimidinone **2** as a transient intermediate in the photochemical reactions of 4-pyrimidinone **1** in protic solvents.[5] We now report the successful isolation of the interesting reactive molecular species.

Irradiation of 4-pyrimidinones **1a–e** in liquid NH_3–ether solution at −40 °C or in methanol[6] at −18 °C gave a mixture of 5-oxo-2,6-diazabicyclo[2.2.0]hex-2-enes (Dewar 4-pyrimidinones) **2a–e** (30–25% estimated by ^1H NMR) and starting materials **1a–e**. The separation of **1** and **2** was carried out by chromatography on Sephadex LH-20 at 17–19 °C with chloroform–hexane (80:20 v/v %) as an

Chart I



1 2

Table I. Isolated Yields and IR Spectral Data for Dewar 4-Pyrimidinones 2

					IR (in $CHCl_3$), cm^{-1}	
no.	R^1	R^2	R^3	yield, %	ν (C=O)	ν (C=N)
2a	CH_3	CH_3	CH_3	24	1750[a]	1605
2b	CH_3	CH_3	*t*-Bu	21	1750	1595
2c	$PhCH_2$	CH_3	*t*-Bu	17	1750	1590
2d	$-(CH_2)_4-$		*t*-Bu	16	1745	1595
2e	H	CH_3	CH_3	0[b]	1750[c]	nd[d]

[a] Reference 5c. [b] A pale yellow polymeric compound (21 w/w %) was obtained and the starting material **1e** (68%) was recovered. [c] Reference 5d. [d] Not determined.

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(6) Irradiation of **1e** was carried out in methanol at −18 °C.[5d]

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