JOC Article

Furan Forming Reactions of *cis*-2-Alken-4-yn-1-ones

Charles P. Casey* and Neil A. Strotman

Department of Chemistry, University of Wisconsin–Madison, Madison, Wisconsin 53706

casey@chem.wisc.edu

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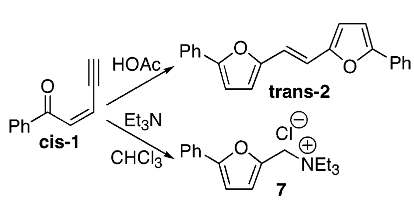


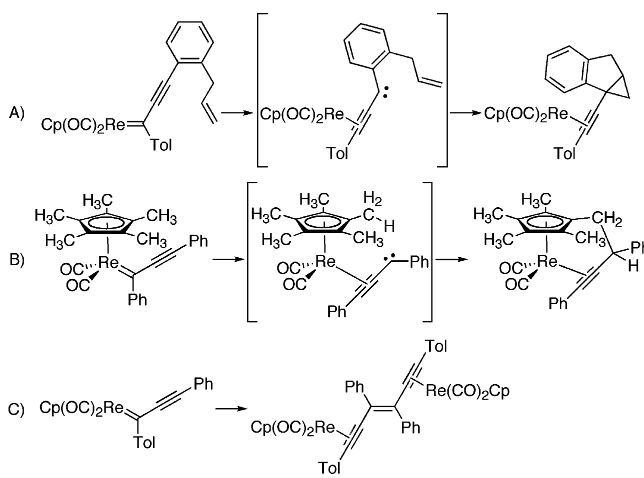
The *cis*-2-alken-4-yn-1-one, 1-phenyl-*cis*-2-penten-4-yn-1-one (*cis*-**1**), readily dimerizes on treatment with weak acid to give the 1,2-difurylethylenes, *trans*- and *cis*-1,2 di(2-(5-phenylfuryl))ethene (*trans*-**1** and *cis*-**2**), in 62% and 23% yields, respectively. Trimerization of *cis*-**1** to *trans*,*trans*-1,2,3-tri(2-(5-phenylfuryl)cyclopropane (**4**) occurred as a byproduct of treatment with weak acid. These reactions demonstrate the 2-furylcarbenoid reactivity of *cis*-2-alken-4-yn-1-ones.

Introduction

Rhenium alkynylcarbene complexes exhibit high reactivity at the remote alkyne carbon. We have observed (A) intramolecular cyclopropanation by addition of the remote alkyne carbon to a tethered alkene,[1] (B) insertion of the remote alkyne carbon into a CH bond of a Cp* ligand,[2] and (C) dimerization by coupling of the remote alkynyl carbons of two molecules[1,3] (Scheme 1). All three reactions can be understood in terms of a [1,1.5] rhenium migration producing "free carbene" character at the remote alkyne carbon.

To investigate carbenoid reactivity at the remote alkyne carbon of rhenium alkynylcarbene complexes, we set out to synthesize carbene complex **A**, which has an enone substitutent on the alkyne (Scheme 2). It has been previously demonstrated that 4-oxabutadienyl carbenes undergo 6π electrocyclizations to form furans.[4] For example, cyclization of a 4-oxabutadienyl carbene, generated via photolysis of the corresponding diazo species, gave a furan (Scheme 3).[4a] We wondered whether the carbenoid reactivity produced at the remote alkynyl carbon of a rhenium alkynylcarbene complex **A** might lead to formation of furan **B** (Scheme 2).

SCHEME 1



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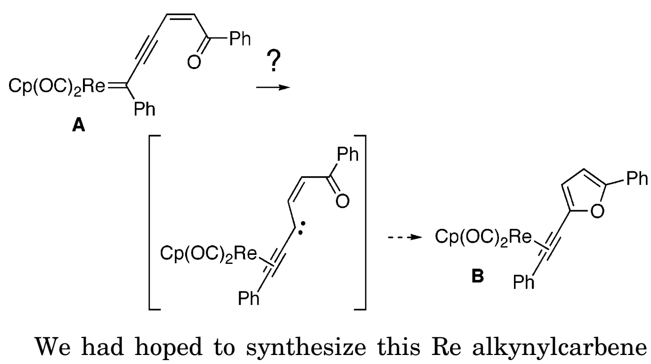

We had hoped to synthesize this Re alkynylcarbene complex **A** by reaction of the appropriate copper acetylide

(1) Casey, C. P.; Kraft, S.; Powell, D. R. *J. Am. Chem. Soc.* **2000**, *122*, 3771.
(2) Casey, C. P.; Kraft, S.; Kavana, M. *Organometallics* **2001**, *20*, 3795.
(3) (a) Casey, C. P.; Kraft, S.; Powell, D. R. *Organometallics* **2001**, *20*, 2651. (b) Casey, C. P.; Kraft, S.; Powell, D. R. *J. Am. Chem. Soc.* **2002**, *124*, 2584.
(4) (a) Tomer, K. B.; Harrit, N.; Rosenthal, I.; Buchardt, O.; Kumler, P. L.; Creed, D. *J. Am. Chem. Soc.* **1973**, *95*, 7402. (b) Padwa, A.; Akiba, M.; Chou, C. S.; Cohen, L. *J. Org. Chem.* **1982**, *47*, 183. (c) Nakatani, K.; Adachi, K.; Tanabe, K.; Saito, I. *J. Am. Chem. Soc.* **1999**, *121*, 8221.

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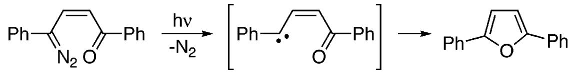
SCHEME 3



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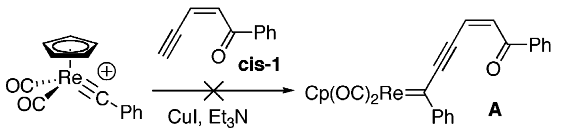

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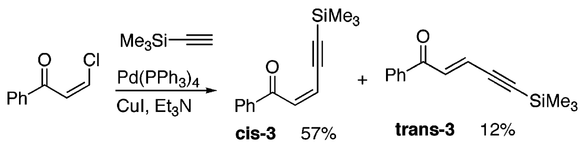


with the Re carbyne complex, $Cp(CO)_2Re{\equiv}CPh^+ BCl_4^-$ (Scheme 4). However, synthesis of **A** was not achieved and no organometallic species were isolated. When 1-phenyl-*cis*-2-penten-4-yn-1-one (*cis*-**1**) and NEt_3 were added to a mixture of the carbyne complex and CuI in CH_2Cl_2, *cis*-**1** was rapidly destroyed and no identifiable product was obtained, except for a small amount of 1-phenyl-*trans*-2-penten-4-yn-1-one (*trans*-**1**) from cis−trans isomerization (Scheme 4).

Here we describe novel thermal reactions of the *cis*-alkenynone *cis*-**1** to give unanticipated furan products. Alkenynone *cis*-**1** readily dimerized in the presence of weak acid to give the 1,2-difurylethylenes, *trans*- and *cis*-1,2-di(2-(5-phenylfuryl))ethene (*trans*-**2** and *cis*-**2**), without metal catalysis or photolysis. Acid-catalyzed reaction of *cis*-**1** also produced the trimer, *trans,trans*-1,2,3-tri(2-(5-phenylfuryl)cyclopropane (**4**). Reaction of *cis*-**1** with Et_3N in $CHCl_3$ gave two additional furan products. In the reactions of *cis*-**1**, the terminal alkynyl carbon functions both as a nucleophile and as an electrophile in furan forming reactions. In this respect, *cis*-**1** behaves as a net (2-furyl)carbenoid.

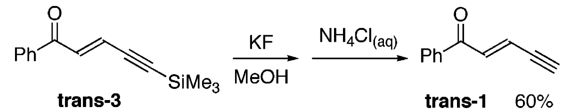
Results and Discussion

Synthesis and Reactivity of 1-Phenyl-*cis*-2-penten-4-yn-1-one (*cis*-1). Palladium-catalyzed Sonagashira coupling of 3-chloro-*cis*-2-propen-1-one[5] with trimethylsilylacetylene gave 1-phenyl-5-trimethylsilyl-*cis*-2-penten-4-yn-1-one (*cis*-**3**) and 1-phenyl-5-trimethylsilyl-*trans*-2-penten-4-yn-1-one (*trans*-**3**) (Scheme 5). *cis*-**3** and *trans*-**3** were separated by flash column chromatography and isolated in 57% and 12% yields, respectively.

trans-**3** was deprotected cleanly with KF in MeOH and workup with aqueous NH_4Cl provided *trans*-**1** in a 60% yield as a yellow solid following flash column chromatography (Scheme 6). *cis*-**1** was prepared in 90% yield by deprotection of *cis*-**3** with KF in MeOH followed by a water quench (Scheme 7). However, when *cis*-**3** was deprotected and quenched with $NH_4Cl_{(aq)}$ instead of water, no *cis*-**1** was observed; the only isolated product was the dimer, *trans*-1,2-di(2-(5-phenylfuryl))ethene (*trans*-**2**) (53% yield).

(5) (a) Muzart, J.; Ajjou, A. N. *Synthesis* **1993**, 785. (b) Ma, S.; Lu, X.; Li, Z. *J. Org. Chem.* **1992**, *57*, 709.

SCHEME 6



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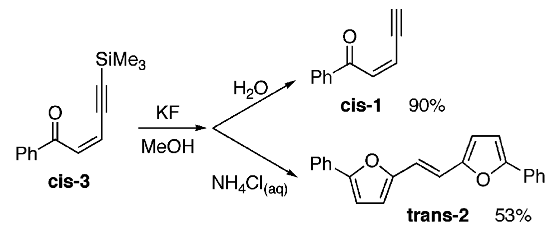

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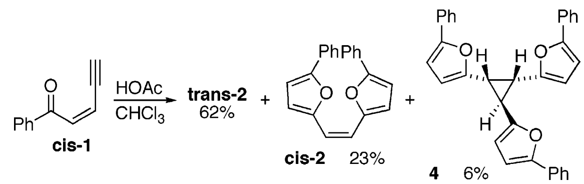


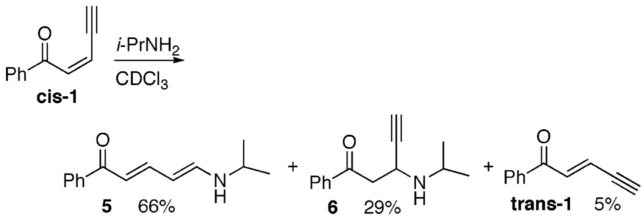
The profound change in reactivity seen when NH_4Cl was introduced prompted us to investigate the role of acid and base in this dimerization process. To probe the effects of acid on this transformation, a solution of *cis*-**1** in $CDCl_3$ was divided and placed in two NMR tubes and 1 equiv of HOAc was added by syringe to one of the tubes. Dimerization of *cis*-**1** to *trans*-**2** occurred over 10 times faster in the presence of acid.

When the reaction of *cis*-**1** in the presence of 2−3 equiv of HOAc in MeOH or $CHCl_3$ was run on a preparative scale, three products were formed in reproducible ratios: dimer *trans*-**2** (62%), a second dimer *cis*-1, 2-di-(2-(5-phenylfuryl))ethene (*cis*-**2**) (23%), and cyclopropane trimer *trans,trans*-1,2,3-tri(2-(5-phenylfuryl))-cyclopropane (**4**) (6%) (Scheme 8). Dimer *trans*-**2** and trimer **4** were separated and isolated by preparative TLC and were spectroscopically characterized. Dimer *cis*-**2** was isolated as a ~1:1 mixture with *trans*-**2** and was characterized spectroscopically as part of this mixture. Isolation of *cis*-**2** proved challenging since it rapidly isomerized to *trans*-**2** in solution. This isomerization might be attributed to light-induced generation of DCl from the NMR solvent.

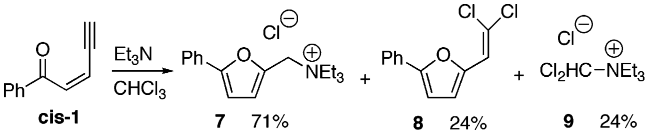
Prior to demonstrating the effects of acid on dimerization to **2**, it had been considered whether dimerization might be base catalyzed. Addition of 1 equiv of isopropylamine to a solution of *cis*-**1** in $CDCl_3$ did not produce dimer **2**. Instead, NMR spectroscopy showed the formation of a small amount (5%) of cis−trans isomerization product *trans*-**1**, as well as substantial amounts of the enamine, 5-isopropylamino-1-phenyl-*trans,trans*-2,4-pentadien-1-one (**5**) (66%), and of the propargylamine, 3-isopropylamino-1-phenyl-4-pentyn-1-one (**6**) (29%) (Scheme 9). Enamine **5** and *trans*-**1** were separated and isolated by preparative TLC, while propargylamine **6** decomposed upon attempted isolation giving more *trans*-**1**. ^1H NMR spectroscopic data for **6** were obtained from the crude mixture of products.

Enamine **5** is the product of 1,6-conjugate addition of isopropylamine to *cis*-**1**, while propargylamine **6** results

SCHEME 9



SCHEME 10

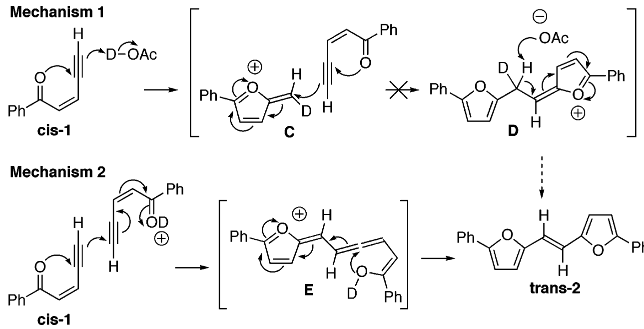


from 1,4-conjugate addition. Isomerization of *cis*-**1** to *trans*-**1** most likely occurs by reversible addition of isopropylamine to C3 of *cis*-**1**. The formation of **6** is also reversible; attempted purification of **6** led to elimination of isopropylamine and formation of additional *trans*-**1**.

To avoid addition products, we switched to a tertiary amine as the base. Reaction of *cis*-**1** with 1 equiv of Et_3N in $CDCl_3$ gave rise to a series of unexpected products, but no dimer was formed. The solution turned black in ~5 min and after 6−10 h, NMR spectroscopy showed the formation of three products: triethyl-(2-(5-phenylfuryl))-ammonium chloride (**7**) (71%), 5-(2,2-dichloroethenyl)-2-phenylfuran (**8**) (24%), and *N*-(dichloromethyl)triethylammonium chloride (**9**)[6] (24%, based on Et_3N) (Scheme 10). **7** and **9** were separated by careful recrystallization, while **8** was purified by preparative TLC. Each compound was characterized by ^1H and ^{13}C NMR spectroscopy as well as by HRMS. *trans*-**1** did not undergo any furan forming reactions with Et_3N, though the acetylenic proton exchanged almost completely with the deuterium of the $CDCl_3$ within a few hours.

Mechanism of Dimerization. We considered two possible mechanisms for acid-catalyzed dimerization of *cis*-**1** (Scheme 11). Mechanism 1 begins with an electrophilic addition of H^+ and the carbonyl oxygen across the C≡C triple bond of *cis*-**1** to give furyl stabilized carbocation **C**. Note that in this reaction the terminal alkyne carbon acts as a nucleophile. The second step involves a similar electophilic addition across the C≡C triple bond of *cis*-**1** to give cation **D**; in this case, the electrophile is furyl stabilized carbocation **C** and the nucleophile is again the terminal alkyne carbon of *cis*-**1** assisted by the carbonyl. Finally, deprotonation of **D** produces the difurylethylene *trans*-**2**.

SCHEME 11



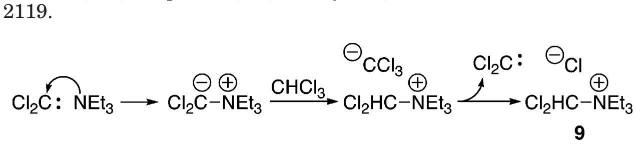
Mechanism 2 begins with protonation of the carbonyl oxygen of *cis*-**1**, which enhances the electrophilic character of the terminal alkyne carbon (Scheme 11). Electrophilic addition to a second molecule of *cis*-**1** then occurs; the electrophile is the terminal alkyne carbon of protonated *cis*-**1** and the nucleophile is again the terminal alkyne carbon of *cis*-**1**, assisted by the carbonyl oxygen. This results in formation of enol intermediate **E**, which can cyclize and then lose a proton to give *trans*-**2**. Both mechanisms are consistent with the observation that *cis*-**1** dimerizes but *trans*-**1** does not, since only *cis*-**1** is poised for addition of the carbonyl oxygen to the C≡C triple bond.

These two mechanisms can be readily differentiated by deuterium labeling studies of the dimerization of *cis*-**1** catalyzed by 3 equiv of DOAc (Scheme 11). In Mechanism 2, the triple bond of *cis*-**1** is never protonated and deuterium should not be found in *trans*-**2**. Mechanism 1 predicts incorporation of a minimum of 0.5 deuterium per dimer *trans*-**2**. Greater deuterium incorporation might occur (1) if protonation of the terminal alkyne carbon to give **C** were reversible, which could lead to deuterium exchange into the *cis*-**1**, or (2) if there is a kinetic isotope effect on deprotonation of **C**.

The reaction of *cis*-**1** with DOAc in $CDCl_3$ produced *trans*-**2,** which was isolated, purified, and carefully analyzed by ^1H NMR spectroscopy. Careful integration of the two sets of furyl protons and the vinyl protons of *trans*-**2** showed a ratio 2.00:1.99:1.88. This indicates 0.12 D at the vinyl position of *trans*-**2**, well below the minimum of 0.50 D required by Mechanism 1. This eliminates Mechanism 1 from consideration and provides strong support that Mechanism 2 is the dominant pathway.

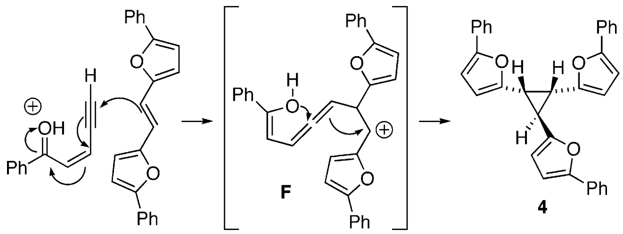
The incorporation of 0.12 D into *trans*-**2** is the result of some exchange of deuterium onto the terminal alkyne carbon of *cis*-**1**. When the reaction of *cis*-**1** with DOAc in $CDCl_3$ was monitored by ^1H NMR spectroscopy, evidence was obtained that about 20% deuterium was incorporated into the acetylenic position of *cis*-**1** after about 90% conversion to *trans*-**2**. This percentage deuterium incorporation was determined by integrating the portion of the vinylic proton at C2 coupled to the acetylenic proton [δ 6.198 (dd, J = 11.6, 2.6 Hz, 0.80H)] versus the portion not coupled to the acetylenic proton [δ 6.197 (d, J = 11.8 Hz, 0.20H)] in the 250 MHz ^1H NMR spectrum.[7] For each doublet (J = 2.6 Hz) corresponding to the proton at C2 of the protio compound, a peak could

(6) We suggest that the formation of **9** is initiated by attack of Et_3N on $:CCl_2$ to give a nitrogen ylide intermediate. Subsequent protonation of the nitrogen ylide by $CHCl_3$ would produce **9** and CCl_3^-. The equilibrium between CCl_3^- and $:CCl_2$ and Cl^- provides a way to regenerate $:CCl_2$. In the absence of *cis*-**1**, no reaction between Et_3N and $CDCl_3$ was seen by ^1H NMR spectroscopy. The Et_3N-mediated two-phase reaction of $NaOH_{(aq)}$ with $CHCl_3$ and an alkene gives a 1,1-dichlorocyclopropane from addition of $:CCl_2$ to the alkene. The same nitrogen ylide, Et_3NCCl_2, was proposed to be involved in this reaction. Makosza, M.; Kacprowicz, A.; Fedorynski, M. *Tetrahedron Lett.* **1975**, 2119.



(7) See the Supporting Information for an expansion of this region of the ^1H NMR spectrum.

SCHEME 12



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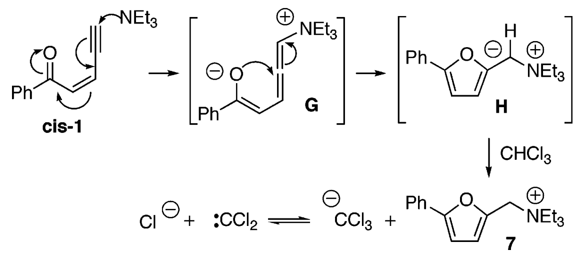
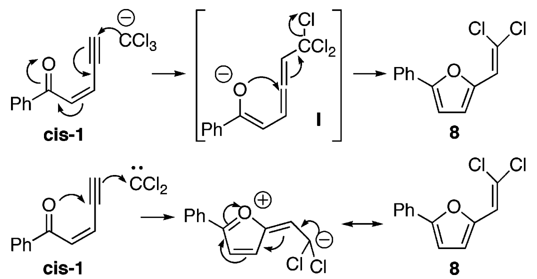


SCHEME 14



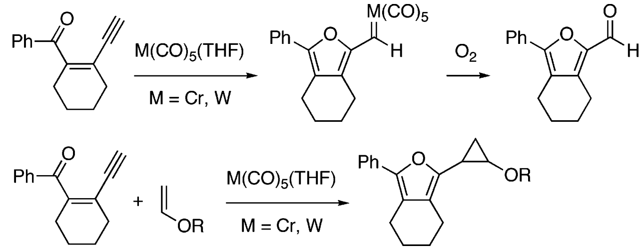
be seen in the middle of the doublet corresponding to the proton at C2 in the analogue bearing a deuterium at the acetylenic proton and not showing long-range coupling. Direct comparison of the acetylenic proton integration to the vinyl proton integration was not possible due to impurity peaks.

Mechanism of Formation of Cyclopropane Trimer 4. We suggest that formation of cyclopropane trimer **4** also begins with protonation of the carbonyl oxygen of *cis*-**1** (Scheme 12). The resulting electrophile then adds to the central C═C double bond of dimer *trans*-**2**, forming stabilized carbocation **F**. Electrophilic addition of the carbocation and of the enol oxygen across the allene unit of **F** forms the cyclopropane and simultaneously closes the third furan ring.

Mechanism of Other Furan-Forming Reactions. We suggest that formation of **7** is initiated by 1,6-conjugate nucleophilic addition of Et_3N to *cis*-**1** to give zwitterionic enolate **G** (Scheme 13). The enolate oxygen of **G** then adds to the vinylammonium unit to form the furan ring and produce nitrogen ylide **H**. Protonation of ylide **H** by $CHCl_3$ produces **7**. The resulting trichloromethyl anion is known to reversibly dissociate chloride to form dichlorocarbene (:CCl_2).

We envision two possible pathways for formation of the dicholorovinyl substituted furan **8**. The first begins with generation of the trichloromethyl anion by deprotonation of $CHCl_3$ by either NEt_3 or intermediate **H** in Scheme 13. 1,6-Conjugate addition of CCl_3 to *cis*-**1** would produce enolate **I** (Scheme 14). Intramolecular attack of the enolate oxygen on the cental allene carbon of **I** could then displace chloride to form **8** in an S_n2' reaction. An alternative route to **8** involves electrophilic addition of :CCl_2 and the carbonyl oxygen across the triple bond of *cis*-**1** to produce **8** directly. Dichlorocarbene could be formed by loss of chloride from trichloromethyl anion generated during the formation of **7** or by Et_3N deprotonation of $CHCl_3$.

SCHEME 15



Carbenoid Reactivity of *cis*-2-Alken-4-yn-1-ones. The furan containing products of the reaction of *cis*-**1** are those expected from a 2-furylcarbene: formal carbene dimerization to *trans*-**2** and *cis*-**2**, cyclopropanation of **2** to give **4**, carbene coupling with :CCl_2 to give dichlorovinyl furan **8**, and formal addition of Et_3N to give an ylide precursor to ammonium salt **7**. Carbenoids show both electrophilic and nucleophilic character at the same carbon, and *cis*-**1** displays just this kind of reactivity pattern at the terminal alkyne carbon. The terminal carbon of the enynone *cis*-**1** is a natural electrophile; this is most clearly shown in the 1,6-conjugate addition of isopropylamine to *cis*-**1** to produce **5** (Scheme 9). Protonation of the carbonyl carbon of *cis*-**1** increases the electophilic character of the terminal alkyne carbon so that even weak nucleophiles such as neutral *cis*-**1** and dimer **2** add to this carbon (Schemes 11 and 12). The terminal carbon of *cis*-**1** can also act as a nucleophile, particularly toward strong electrophiles such as protonated *cis*-**1** or :CCl_2 (Schemes 11 and 14). Since only the cis isomer shows this nucleophilic character, simultaneous attack of the carbonyl oxygen of *cis*-**1** at the internal alkyne carbon to generate a furan ring undoubtedly enhances the nucleophilic reactivity of the terminal alkyne carbon.

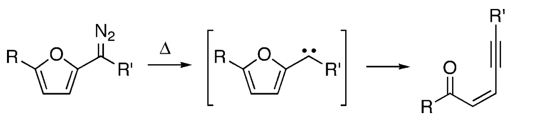
Relationship to Metal Mediated Furan Formation. The reaction of a *cis*-2-alken-4-yn-1-one with $M(CO)_5$-(THF) provides an interesting route to (2-furyl)carbene chromium (or tungsten) complexes (Scheme 15).[8] These cyclizations can be viewed as an electrophilic addition across the C≡C triple bond; the electrophilic metal adds to the terminal alkyne carbon as the ketone carbonyl adds to internal alkyne carbon. In effect, the *cis*-2-alken-4-yn-1-one acts as a (2-furyl)carbenoid that adds to the metal center. These metal carbene complexes were subsequently oxidized by dioxygen to give furfurals. When the carbene complexes were generated from $M(CO)_5$-(THF) and a *cis*-2-alken-4-yn-1-one in the presence of electron-rich alkenes, (2-furyl)cyclopropanes were formed catalytically.[9]

Relationship to Thermal Ring Opening of 2-Furylcarbenes to *cis*-2-Alken-4-yn-1-ones. The ther-

(8) Miki, K.; Yokoi, T.; Nishino, F.; Ohe, K.; Uemura, S. *J. Organomet. Chem.* **2002**, *645*, 228.

(9) (a) Miki, K.; Nishino, F.; Ohe, K.; Uemura, S. *J. Am. Chem. Soc.* **2002**, *124*, 5260. (b) Miki, K.; Yokoi, T.; Nishino, F.; Kato, Y.; Washitake, Y.; Ohe, K.; Uemura, S. *J. Org. Chem.* **2004**, *69*, 1557.

SCHEME 16



mal extrusion of N_2 from 1-diazo-1-(2-furyl)alkanes, designed to generate the corresponding 1-(2-furyl)-1-alkylcarbenes, gave rearranged 2-alken-4-yn-1-ones (Scheme 16).[10] This reaction represents the microscopic reverse of cyclization of a *cis*-2-alken-4-yn-1-one to give a 2-furylcarbene. While our furan-forming reactions do not proceed through free high energy 2-furylcarbene intermediates, the products are those expected from such a carbenoid.

Experimental Section

1-Phenyl-5-trimethylsilyl-*cis*-2-penten-4-yn-1-one (*cis*-3) and 1-Phenyl-5-trimethylsilyl-*trans*-2-penten-4-yn-1-one (*trans*-3). Toluene (32 mL), Et_3N (1.60 mL, 11.5 mmol), and *cis*-3-chloro-1-phenyl-2-propen-1-one[5] (1.00 g, 6.00 mmol) and then (trimethylsilyl)acetylene (1.06 mL, 7.50 mmol) were added by syringe to a flask containing CuI (57 mg, 0.30 mmol) and $Pd(PPh_3)_4$ (139 mg, 0.120 mmol). The mixture was stirred at room temperature under N_2 for 7 h, quenched with saturated aqueous ammonium chloride (27 mL), and extracted with EtOAc (3 × 15 mL). The extract was dried ($MgSO_4$) and concentrated on a rotary evaporator, and chromatographed (silica gel, 100:4 pentane:ether) to give *cis*-**3** (0.79 g, 57% yield) as a brown oil and *trans*-**3** (0.16 g, 12%) as a tan solid. For *cis*-**3**: ^1H NMR (300 MHz, $CDCl_3$) δ 7.94 (dd, J = 8.5, 1.7 Hz, 2H), 7.57 (tt, J = 7.4, 1.4 Hz, 1H), 7.46 (t, J = 7.5 Hz, 2H), 6.97 (d, J = 12.0 Hz, 1H), 6.22 (d, J = 11.7 Hz, 1H), 0.13 (s, 9H). ^{13}C {^1H} NMR (75 MHz, $CDCl_3$) δ 190.8, 137.8, 135.0, 133.2, 129.0 (2C), 128.8 (2C), 120.9, 107.8, 101.8, −0.3 (3C). HRMS (ESI) calcd for $C_{14}H_{16}OSiNa$ (M + Na^+) 251.0868, found 251.0866. For *trans*-**3**: ^1H NMR (300 MHz, $CDCl_3$) δ 7.96 (dd, J = 8.4, 1.5 Hz, 2H), 7.59 (tt, J = 7.4, 1.4 Hz, 1H), 7.48 (t, J = 7.7 Hz, 2H), 7.38 (d, J = 15.6 Hz, 1H), 6.88 (d, J = 15.6 Hz, 1H), 0.25(s, 9H). ^{13}C {^1H} NMR (75 MHz, $CDCl_3$) δ 189.0, 137.3, 134.4, 133.4, 128.9 (2C), 128.8 (2C), 106.1, 102.8, −0.2 (3C). HRMS (ESI) calcd for $C_{14}H_{16}OSiH$ (M + H^+) 229.1049, found 229.1047.

1-Phenyl-*trans*-2-penten-4-yn-1-one (*trans*-1). A solution of *trans*-**3** (250 mg,1.09 mmol) and anhydrous KF (0.43 g, 7.3 mmol) in MeOH (10 mL) was stirred at room temperature for 2 h, poured into $NH_4Cl_{(aq)}$ (20 mL), and extracted with EtOAc (3 × 15 mL). The organic layer was washed with water (3 × 10 mL), dried ($MgSO_4$), and concentrated by rotary evaporation. Flash column chromatography (silica gel, 20:1 pentane:ether) gave *trans*-**1** (103 mg, 60%) as a pale yellow powder. ^1H NMR (300 MHz, $CDCl_3$) δ 7.96 (d, J = 6.9 Hz, 2H), 7.60 (tt, J = 7.4, 1.4 Hz, 1H), 7.49 (t, J = 7.5 Hz, 2H), 7.44 (dd, J = 15.9, 0.6 Hz, 1H), 6.85 (dd, J = 15.6, 2.7 Hz, 1H), 3.45 (dd, J = 2.7, 0.7 Hz, 1H). ^{13}C {^1H} NMR (75 MHz, $CDCl_3$) δ 188.8, 137.1, 135.5, 133.6, 129.0 (2 C), 128.8 (2 C), 124.0, 86.7, 81.6; HRMS (ESI) calcd for $C_{11}H_8ONa$ (M + Na^+) 179.0473, found 179.0478.

1-Phenyl-*cis*-2-penten-4-yn-1-one (*cis*-1). A solution of *cis*-**3** (250 mg,1.09 mmol) and anhydrous KF (0.43 g, 7.3 mmol) in MeOH (10 mL) was stirred at room temperature for 2 h. Et_2O (200 mL) was added and the solution was washed with water (2 × 40 mL), dried ($MgSO_4$), and concentrated on a rotary evaporator to give *cis*-**1** (0.154 g, 90%, >95% *cis*-**1** by NMR) as a yellow-brown oil. This oil was chromatographed (silica gel, 20:1 pentane:ether) to afford *cis*-**1** (25 mg, 14%) as a yellow solid, though there was extensive dimerization and material loss on the column. In most cases the crude brown oil was used for reactions. ^1H NMR (300 MHz, $CDCl_3$)[9a] δ 7.97 (d, J = 8.0 Hz, 2H), 7.59 (tt, J = 7.3, 1.2 Hz, 1H), 7.48 (t, J = 7.7 Hz, 2H), 7.20 (dd, J = 11.7, 0.9 Hz, 1H), 6.21 (dd, J = 11.6, 2.6 Hz, 1H), 3.51 (dd, J = 2.7, 1.2 Hz, 1H). ^{13}C {^1H} NMR (75 MHz, $CDCl_3$) δ 189.4, 137.4, 135.5, 133.5, 128.9 (2 C), 128.8 (2 C), 120.3, 88.3, 80.8.

***trans*-1,2-Di(2-(5-phenylfuryl))ethene (*trans*-2), *cis*-1,2-Di(2-(5-phenylfuryl))ethene (*cis*-2), and *trans,trans*-1,2,3-Tri(2-(5-phenylfuryl))cyclopropane (4).** A solution of *cis*-**3** (250 mg,1.09 mmol) and anhydrous KF (0.43 g, 7.3 mmol) in MeOH (10 mL) was stirred at room temperature for 2 h, poured into $NH_4Cl_{(aq)}$ (20 mL), and extracted with EtOAc (3 × 15 mL). The organic layer was washed with water (3 × 10 mL), dried ($MgSO_4$), and concentrated by rotary evaporation. This crude product was dissolved in $CDCl_3$ and the percent yields of *trans*-**2** and *cis*-**2** were determined to be 53% and 10%, respectively, by ^1H NMR spectroscopy relative to an added internal standard.

The yield of **2** was increased by use of an acid catalyst. A solution of *cis*-**1**, obtained from deprotection of *cis*-**3** (50 mg, 0.219 mmol) as described above, and HOAc (19 μL, 0.33 mmol) in $CDCl_3$ (~0.75 mL) was monitored by ^1H NMR spectroscopy. After 1.5 h, the reaction was complete and *trans*-**2** (62%), *cis*-**2** (23%), and **4** (6%) were seen.

Reaction of *cis*-**1** (100 mg, 0.438 mmol) and HOAc (38 μL, 0.66 mmol) in either MeOH or $CHCl_3$ followed by purification by preparative TLC (silica gel, 5:1 pentane:CH_2Cl_2) gave **4** as a yellow oil (R_f 0.25). ^1H NMR (300 MHz, $CDCl_3$) δ 7.65 (d, J = 8.3 Hz, 2H), 7.55 (d, J = 8.3 Hz, 4H), 7.38 (t, J = 7.2 Hz, 2H), 7.22−7.31 (m, 5H), 7.17 (tt, J = 7.2, 1.2 Hz, 2H), 6.62 (d, J = 3.3 Hz, 1H), 6.49 (d, J = 3.6 Hz, 2H), 6.32 (d, J = 3.3 Hz, 1H), 6.11 (d, J = 3.3 Hz, 2H), 3.17 (t, J = 5.7 Hz, 1H), 3.00 (d, J = 5.7 Hz, 2H). ^{13}C {^1H} NMR (75 MHz, $CDCl_3$) δ 153.1, 152.9 (2C), 152.8, 151.2 (2C), 131.1 (2C), 131.0, 128.9 (2C), 128.7 (4C), 127.3, 127.1 (2C), 123.72 (2 C), 123.70 (4 C), 109.4 (2C), 107.9, 106.3, 106.1 (2C), 25.7 (2C), 23.3. HRMS (EI) calcd for $C_{33}H_{24}O_3$ (M^+) 468.1725, found 468.1714.

trans-**2** (55 mg, 55%) and *cis*-**2** coeluted (R_f 0.39) and were further separated by recrystallization from acetone to give yellow solids. *trans*-**2** (decomposition at 208−210 °C before melting) was obtained in a pure state. ^1H NMR (300 MHz, $CDCl_3$) δ 7.73 (d, J = 7.2 Hz, 4H), 7.40 (t, J = 7.5 Hz, 4H), 7.27 (tt, J = 7.5, 1.2 Hz, 2H), 6.93 (s, 2H), 6.71 (d, J = 3.6 Hz, 2H), 6.45 (d, J = 3.6 Hz, 2H). ^{13}C {^1H} NMR (75 MHz, $CDCl_3$) δ 153.7, 152.9, 130.80, 128.9 (2 C), 127.7, 124.01 (2 C), 114.7, 111.6, 107.76. HRMS (ESI) calcd for $C_{22}H_{16}O_2$ (M^+) 312.1150, found 312.1142.

Solutions of *cis*-**2** completely isomerized to *trans*-**2** in $CDCl_3$ over a few hours or quite rapidly in the presence of light. All NMR data for *cis*-**2** were obtained from a ~1:1 mixture with *trans*-**2**. For *cis*-**2**: ^1H NMR (300 MHz, $CDCl_3$) δ 7.73 (d, J = 7.7 Hz, 4H), 7.37 (t, J = 8.4 Hz, 4H), 7.26 (tt, J = 7.0, 1.2 Hz, 2H), 6.98 (d, J = 3.3 Hz, 2H), 6.77 (d, J = 3.3 Hz, 2H), 6.25 (s, 2H). ^{13}C {^1H} NMR (75 MHz, $CDCl_3$) δ 153.9, 152.4, 130.78, 129.0 (2 C), 127.8, 123.99 (2 C), 113.9, 113.6, 107.78. HRMS (EI) calcd for $C_{22}H_{16}O_2$ (M^+) 312.1150, found 312.1158.

5-Isopropylamino-1-phenyl-*trans,trans*-2,4-pentadien-1-one (5) and 3-Isopropylamino-1-phenyl-4-pentyn-1-one (6). A solution of *cis*-**1**, from deprotection of *cis*-**3** (50 mg, 0.219 mmol), and isopropylamine (37 μL, 0.44 mmol) in $CHCl_3$ (5 mL) was stirred at room temperature for 5 h under N_2. Solvent and excess isopropylamine were evaporated under reduced pressure. ^1H NMR spectroscopy of the crude material showed compounds **5**, **6**, and *trans*-**1** in 66%, 29%, and 5% yields, respectively. Preparative TLC (silica gel, 2:1 EtOAc: hexane) led to the isolation of **5** (30 mg, 64%, R_f 0.54) as an oily brown solid and *trans*-**1** (R_f 0.89). Compound **6** readily decomposed during purification so it was identified by proton NMR from a mixture of species.

(10) (a) Hoffman, R. V.; Shechter, H. *J. Am. Chem. Soc.* **1971**, *93*, 5940. (b) Hoffman, R. V.; Orphanides, G. G.; Shechter, H. *J. Am. Chem. Soc.* **1978**, *100*, 7927. (c) Hoffman, R. V.; Shechter, H. *J. Am. Chem. Soc.* **1978**, *100*, 7934.

Alternatively, compounds **5** and **6** were obtained from reaction of *trans*-**3** (200 mg, 0.88 mmol) and isopropylamine (0.73 mL, 8.8 mmol) in CH_3OH (15 mL) over 5 h. The reaction mixture was dissolved in EtOAc (150 mL), washed with water (60 mL), dried ($MgSO_4$), and concentrated by rotary evaporation. ^{1}H NMR spectroscopy showed a 55:36:9 ratio of compounds **6**:**5**:*trans*-**1**.

For **5**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.92 (d, J = 8.0 Hz, 2H), 7.60 (ddd, J = 14.4, 12.0, 0.6 Hz, 1H), 7.50−7.39 (m, 3H), 6.84 (dd, J = 12.8, 9.5 Hz, 1H), 6.61 (d, J = 14.1 Hz, 1H), 5.49 (dd, J = 12.9, 11.7 Hz, 1H), 4.42 (broad t, J = 7.6 Hz, 1H), 3.55 (octet, J = 6.8 Hz, 1H), 1.22 (d, J = 6.3 Hz, 6H). ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$) δ 190.1, 149.4, 148.4, 140.1, 131.5, 128.4 (2C), 128.1 (2C), 113.4, 99.1, 46.5, 23.0 (2C). HRMS (ESI) calcd for $C_{14}H_{17}NOH$ (M + H$^+$) 216.1388, found 216.1379.

For **6**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.96 (d, J = 7.7 Hz, 2H), 7.60−7.40 (m, 3H), 4.08 (td, J = 6.3, 2.1 Hz, 1H), 3.36 (d, J = 6.3 Hz, 1H), 3.35 (d, J = 6.3 Hz, 1H), 3.18 (septet, J = 6.3 Hz, 1H), 2.26 (d, J = 2.1 Hz, 1H), 1.88 (broad s, 1H), 1.11 (d, J = 6.3 Hz, 3H), 1.06 (d, J = 6.3 Hz, 3H).

Triethyl(2-(5-phenylfuryl))ammonium Chloride (7), 5-(2,2-Dichloroethenyl)-2-phenylfuran (8), and (Dichloromethyl)triethylammonium Chloride (9). When a solution of *cis*-**1**, prepared from *cis*-**3** (50 mg, 0.219 mmol) and Et_3N (30.5 μL, 0.219 mmol) in $CDCl_3$ (5 mL), was stirred for 24 h, the deuterated analogues of **7**, **8**, and **9** were produced in 71%, 24%, and 24% yield, respectively, by NMR.

A solution of *cis*-**1**, prepared from *cis*-**3** (100 mg, 0.438 mmol), and Et_3N (122 μL, 0.876 mmol) in $CHCl_3$ (5 mL) was stirred for 6 h. Solvent and excess Et_3N were evaporated under reduced pressure to give a brown oil. Several small portions of Et_2O were added to wash this practically insoluble oil to extract **8**. Evaporation of Et_2O and preparative TLC (10:1 pentane:ether) gave **8** as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.68 (d, J = 8.3 Hz, 2H), 7.39 (t, J = 8.0 Hz, 2H), 7.29 (tt, J = 7.5, 1.4 Hz, 1H), 6.839 (dd, J = 3.6, 0.6 Hz, 1H), 6.834 (d, J = 0.6 Hz, 1H), 6.73 (d, J = 3.9 Hz, 1H). ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$) δ 154.1, 148.1, 130.3, 129.0 (2C), 128.1, 124.2 (2C), 119.3, 118.5, 113.9, 107.3. HRMS (EI) calcd for $C_{12}H_8Cl_2O$ (M)$^+$ 237.9952, found 237.9947.

The remaining brown oil (from the extraction above), which was insoluble in Et_2O, was dissolved in warm CH_2Cl_2/Et_2O and after successive recrystallizations gave **7** and **9** each as white crystals.

For **7**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.60 (d, J = 7.5, 2H), 7.42 (t, J = 7.5 Hz, 2H), 7.34 (t, J = 7.5 Hz, 1H), 7.03 (d, J = 3.6 Hz, 1H), 6.68 (d, J = 3.3 Hz, 1H), 5.03 (s, 2H), 3.51 (q, J = 7.4 Hz, 6H), 1.53 (t, J = 7.4 Hz, 9H). ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$) δ 156.8, 141.5, 129.6, 129.2 (2C), 128.8, 124.2 (2C), 119.5, 106.6, 54.5, 53.7 (3C), 8.5 (3C). HRMS (ESI) calcd for $C_{17}H_{24}NO$ (M)$^+$ 258.1858, found 258.1848.

For **9**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.04 (s, 1H), 3.95 (q, J = 7.4 Hz, 6H), 1.63 (t, J = 7.4 Hz, 9H). ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$) δ 90.8, 55.9 (3C), 10.2 (3C). HRMS (ESI) calcd for $C_7H_{16}Cl_2N^+$ (M)$^+$ 184.0660, found 184.0666.

Dimerization of *cis*-1 Catalyzed by DOAc. A solution of *cis*-**1**, from deprotection of *cis*-**3** (50 mg, 0.219 mmol), and DOAc (37.9 μL, 0.657 mmol) in $CDCl_3$ (~0.5 mL) was shaken in an NMR tube and immediately placed in the spectrometer. After 85 min, the reaction had reached 90% completion and the acetylenic position of *cis*-**1** contained 20% deuterium. After 115 min, >97% of *cis*-**1** had reacted and the solution was washed with water to remove the DOAc. $CDCl_3$ was evaporated and the solid residue was washed with acetone to give *trans*-**2** as a yellow solid. The extent of deuteration was determined by ^{1}H NMR spectroscopy. The two vinyl protons of *trans*-**2** (δ 6.93) integrated as 1.88H relative to the two sets of furyl protons of *trans*-**2** (δ 6.71 and 6.45), which integrated as 2.00H and 1.99H, respectively.

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Supporting Information Available: ^{13}C NMR spectra for compounds *cis*-**1**, *trans*-**1**, *trans*-**2**, *cis*-**3**, *trans*-**3**, **4**, **5**, **7**, **8**, and **9** and a ^{1}H NMR spectrum for compound *cis*-**2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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