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Formation of Allenyl Ketones, 3-Ethynylcoumarins, and Arylfurans, Furylfurans, and Furylthiophenes by Flash Vacuum Thermolysis of 3-Methylidenefuran-2(3*H*)-ones

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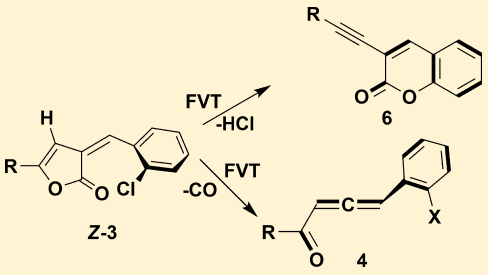
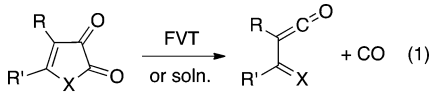
Supporting Information

ABSTRACT: Flash vacuum thermolysis (FVT) of 3-methylidenefuran-2(3*H*)-ones **3** causes cheletropic extrusion of CO with formation of allenyl ketones **4**. *o*-Chloro- and *o*-bromophenylmethylidenefuranones also afford allenyl ketones upon flash vacuum thermolysis, but in addition, 3-ethynylcoumarins **6** are formed via *E*/*Z* isomerization of the methylidenefuranones, cyclization, halogen atom migration, and HCl (HBr) elimination. The presence of strongly electron-withdrawing groups (nitroaryl or acetyl) on the acylallene moiety causes rearrangement to give 2-arylfurans **10** and **13** as well as 2-furylfurans and 2-furylthiophenes **16** by cyclization of the allenyl ketones. The reaction mechanisms are supported by calculations at the M06-2X/6-311+G(d,p) level of theory.

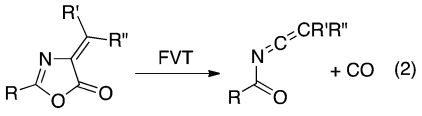


INTRODUCTION

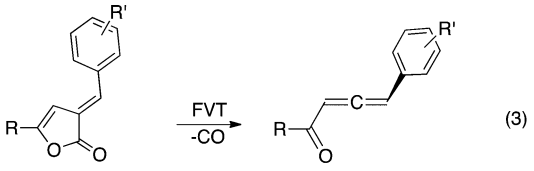
There are many synthetically useful pericyclic fragmentation reactions of five-membered heterocyclic compounds, often taking place under the conditions of flash vacuum thermolysis (FVT). We recently reported a computational analysis of the mechanistic diversity of such reactions, which involve (cheletropic) extrusion of CO, CO_2, or an isocyanate (RNCO).[1] Examples are the formation of acylketenes, thioacylketenes, and imidoylketenes by FVT of furan-, thiophen-, and pyrrole-2,3-diones (eq 1)[2] and of *N*-



X = O, S, or NR



acylketenimines from 4-methylenoxazol-5(4*H*)-ones (eq 2).[3] All of these reactions take place with activation energies ranging from ca. 23 to 50 kcal/mol.[2] In a similar manner, 3-methylenefuran-2(3*H*)-ones **1** undergo extrusion of CO to form 4-arylallenyl ketones **2** upon FVT at ca. 700 °C (eq 3).[3] While these allenes can be isolated at room temperature, they are generally unstable and should be stored below −20 °C. In this paper, we describe competing and sequential reactions of



1 **2**

a R = Ph, R' = H; **b** R = Ph, R' = *p*-MeO; **c** R = Ph, R' = *p*-Cl; **d** R = Ph, R' = *m*-Cl; **e** R = Me, R' = H; **f** R = Me, R' = *p*-MeO; **g** R = Me, R' = *p*-Cl; **h** R = Me, R' = *p*-NO_2; **i** R = Me, R' = *p*-CHO.

furanones **1** leading to the formation of 3-ethynylcoumarins and 2-arylfurans, 2-furylfurans, and 2-furylthiophenes.

EXPERIMENTAL RESULTS

1. Coumarin Formation. FVT of *o*-chlorobenzylidenefuranone **3a** at 750 °C and 10^{-4}−10^{-3} hPa with isolation of the products in a liquid nitrogen trap (−196 °C) afforded two compounds. The first, an acetone-soluble material, was purified by preparative thin-layer chromatography to yield a yellow oil, which was identified as the expected allenyl ketone **4a**, whose spectroscopic properties were fully in accord with those previously published for **2**, including a strong allene absorption at 1938 cm^{-1} in the IR spectrum. The second product crystallized from acetone as slightly yellow needles and was analyzed as $C_{17}H_{10}O_2$. Most tellingly, the IR spectrum featured a very weak absorption at 2215 cm^{-1} and a strong one at 1724

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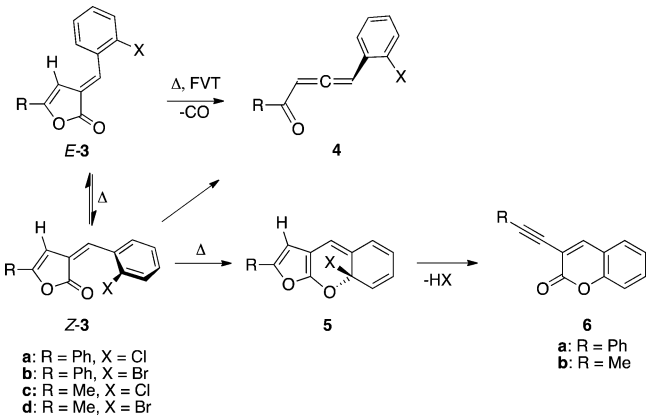
cm^{-1}, whereas the Raman spectrum showed a very strong signal at 2212 cm^{-1} and a weak one at 1713 cm^{-1}, thus indicating the compound to be a disubstituted acetylene containing a carbonyl group. The spectra were in excellent agreement with the calculated IR and Raman spectra at the M06-2X/6-311+G(d,p) level (see Figures S1−S4 in the Supporting Information). These data together with the ^1H and ^{13}C NMR spectra fully identified the compound as 3-(phenylethynyl)coumarin (**6a**) (Scheme 1).

Scheme 1. Formation of Allenes and Coumarins



The 3-arylmethylidenefuran-2(3*H*)-ones **1** and **3** exist in the *E* configuration, as was already determined by Maquestiau et al. on the basis of the fact that the exocyclic proton H6 is deshielded by the neighboring C═O group and therefore resonates at a lower magnetic field than would be expected for the corresponding *Z* isomer.[4] Furthermore, in the 5-methyl derivatives **1e** and **1f** a significant $^6J_{HH}$ coupling of 0.7−0.9 Hz between the methyl group protons and H6 is observed. This can only happen with an all-*trans* relationship between these protons (i.e., the *E* isomer).[2] However, thermal *E*/*Z* isomerization can be expected to take place under the conditions of FVT used to synthesize coumarins **6**, and this was confirmed by the calculations described below. Thus, the formation of **6a** can be ascribed to cyclization of the *Z*-*o*-chlorobenzylidene derivative *Z*-**3a** to give **5** followed by elimination of HCl (Scheme 1). The *m*- and *p*-chloro derivatives **1c** and **1d** cannot undergo this cyclization/elimination reaction, and the expected allenes **2c** and **2d** are formed instead. Mechanistic details of the coumarin-forming reaction are described in the Computational Section.

Similar FVT of the *o*-bromo compound **3b** afforded the same compound **6a** by elimination of CO and HBr. In this case, the expected allene **4b** was not detectable.

FVT of the 5-methyl-3-(*o*-chlorobenzylidene)- and 5-methyl-3-(*o*-bromobenzylidene)furan-2-ones **3c** and **3d** yielded 3-propynylcoumarin (**6b**, $C_{12}H_8O_2$) in each case. Here the IR spectrum shows a weak acetylenic absorption at 2220 cm^{-1}, and the Raman spectrum shows the corresponding band strongly at 2220 cm^{-1}. The ^1H and ^{13}C NMR spectra are fully in accord with structure **6b**. The allenes **4c** and **4d** were detectable by IR absorptions at 1938 and 1935 cm^{-1}, respectively, but were not isolated in a pure state.

2. 2-Aryl- and 2-Heteroarylfuran Formation. Another detour from the standard allene-forming reaction (eq 3) takes place with the nitroaryl-substituted furanones **7**. Here, the allenes **8** formed on FVT were detectable by their characteristic IR absorptions at 1937−1938 cm^{-1}, but the main products were the furans **10** formed by cyclization of the allenes (Scheme 2). On the basis of the calculations described below, the most likely intermediates are the cyclic oxyvinylcarbenes **9** (see Mechanistic Studies). This formation of 2-arylfurans is favored by strongly electron-withdrawing nitroaryl substituents on the allene.

An additional acyl substituent has the same effect, as 4-acetyl-3-benzylidenefuran-2-one **11** and the analogous 3-furylmethylidene and 3-thienylmethylidene derivatives **14a** and **14b** also produced furans **13** and **16**, respectively, as end products (Scheme 3). Here the diacylallene (vinylidenemalonate) intermediates **12** and **15** were detectable only by their weak IR absorptions at 1930−1931 cm^{-1} in the crude products.

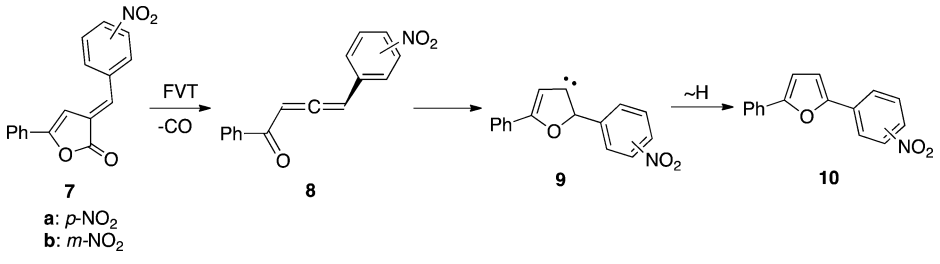
In contrast to furanones **1** and **3**, compounds **11** and **14** have a *Z* orientation of the exocyclic phenyl, furyl, and thienyl substituents, as revealed by the absence of the long-range coupling between the methylidene proton and the CH_3 group in position **5** described above.

MECHANISTIC STUDIES

In order to verify the experimental findings, computations were performed employing the modern and robust M06-2X hybrid functional together with the triple-ξ-quality 6-311+G(d,p) basis set.

In a first step, allene formation via ring opening of furanones *E*-**3** and *Z*-**3** and the cyclization of *Z*-**3** to yield the 8*H*-chromene derivative **5** were investigated for the parent system **3e**−**5e** (R = H, X = H; Scheme 4). While the furanone energies differ by about 2 kcal/mol in favor of *E*-**3**, the two ring-opening processes seem to pass through the same transition state (or almost identical TSs) in which the phenyl ring is oriented almost perpendicular to the plane of the furanone ring (Figure 1). In agreement with the endothermicity of the reaction, this indicates a late transition state in which the perpendicular allene configuration is largely formed. The activation energy is about 60 kcal/mol ($\Delta G^{\ddagger}$ = 55 kcal/mol) leading to the allenyl ketone. This is close to the upper limit of activation barriers calculated

Scheme 2. Formation of 2-Arylfurans 10



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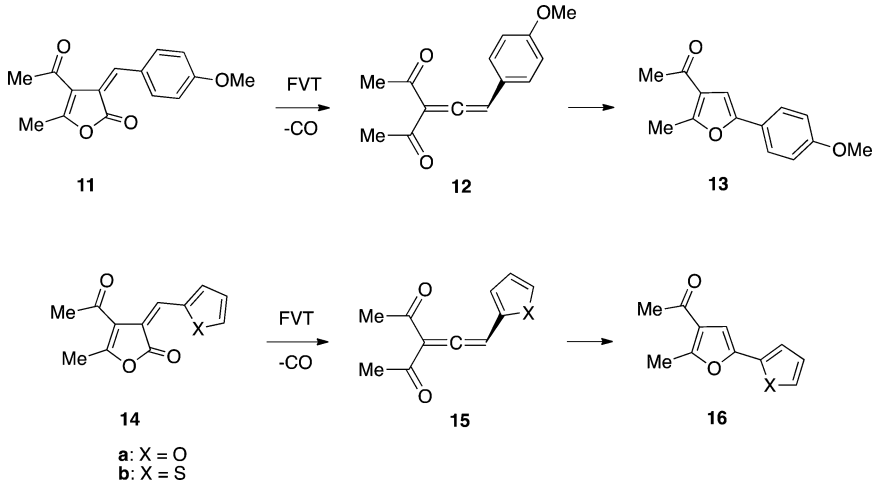
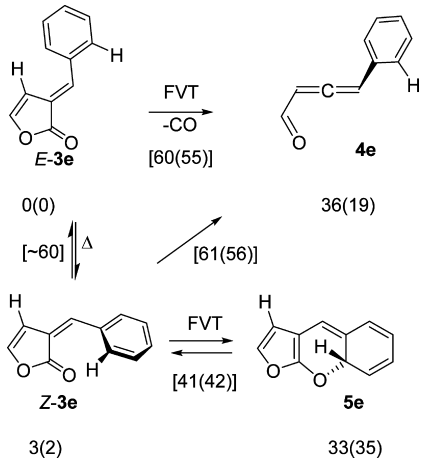
Scheme 3. Formation of 2-Arylfuran 13 and Furylfurans and Furylthiophenes 16



Scheme 4. Possible FVT Reactions of Furanone 3e[a]



[a]Values of ΔE and (in parentheses) ΔG are in kcal/mol and were computed at the M06-2X/6-311+G(d,p) level. Values in brackets are transition state energies.

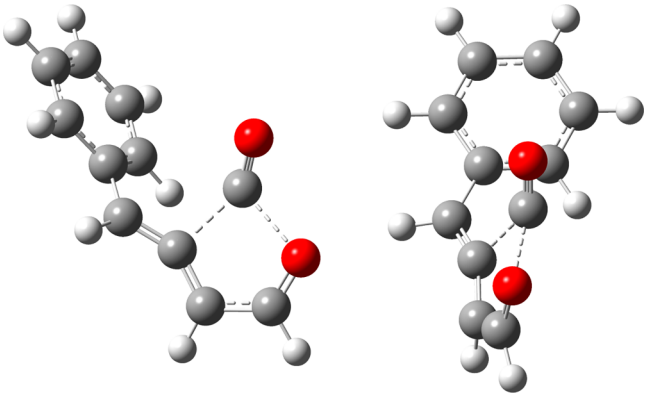


Figure 1. M06-2X/6-311+G(d,p)-optimized transition state for CO extrusion from 3-phenylmethylidenefuran-2(3*H*)-one.

for other CO extrusions.[1] Electrocyclization of *Z*-**3e** requires only about 42 kcal/mol, while the interconversion of *E*- and *Z*-furanone possesses an estimated barrier of 60 kcal/mol. This means that *E*/*Z* isomerization is competitive with CO elimination from the *E* isomer, with the consequence that formation of both allene and coumarin becomes possible.

When these results were compared with data obtained using the popular B3LYP functional and the recent dispersion-corrected ωB97X-D functional, it was found that the (free) energies computed with the recent functionals M06-2X and ωB97X-D are identical within 1 kcal/mol, while B3LYP gives barriers that are higher by as much as 5 kcal/mol (see the Supporting Information for details). This is in line with other related studies[5−7] in which M06-2X results agree better with high-level data. This leads to the assumption that M06-2X/6-311+G(d,p) is a robust and reliable theoretical level for studying these and related reactive species.

The formation of coumarin **6** by FVT of *o*-chlorobenzylidenefuranone **3a** was investigated using the model compounds **3f**–**6f** (R = H, X = Cl; Scheme 5 and Figure 2). In a first step, *Z*-**3f** cyclizes to 8a*H*-furochromene derivative **5f** with a moderate barrier of 38 kcal/mol. This intermediate can easily stabilize itself via a 1,5-chlorine migration leading to the aromatic 9a*H*-furochromene isomer **17**. This reaction requires only about 3 kcal/mol, and the resulting intermediate is 20 kcal/mol more stable than **5f**. Subsequent elimination of HCl (E_a = 51 kcal/mol) leads to the ethynylcoumarin **6f**. Thus, the *E*/*Z* isomerization is the rate-determining step for coumarin formation.

The formation of 2-arylfurans that takes place with the nitroaryl-substituted furanones **7** proceeds via the observable allenyl ketones **8**. From here, several allene cyclization pathways were investigated computationally (Scheme 6): formation of oxyvinylcarbene **18** via a 1,2-H shift, followed by ring closure (route a); ring closure to form cyclic oxyvinylcarbene **19**, which then undergoes a 1,2-H migration (route b); and cyclization of enynol **22**, which is formed either via two consecutive 1,3-H shifts (route c) or a direct 1,5-H migration (route d).[8]

The first route to 2-phenylfuran **20** can be ruled out because of the unfavorable 1,2-hydrogen atom shift leading to the high-energy singlet carbene **18**, which would require a significantly higher activation energy (60 kcal/mol). No transition state for the ring closure to the furan product could located; it therefore appears to be barrierless. Cyclization of **4e** to cyclic carbene **19** (route b), however, is much more feasible. It requires only about 40 kcal/mol and leads to a singlet carbene, and the final 1,2-H shift possesses a barrier of little more than 40 kcal/mol. These barriers are perfectly accessible under FVT conditions.

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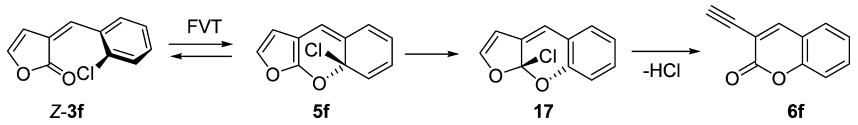
Scheme 5. M06-2X/6-311+G(d,p)-Derived Mechanism of Ethynylcoumarin Formation[a]



[a]Values of ΔE (first row) and ΔG (second row) are in kcal/mol. Values in brackets are transition state energies.

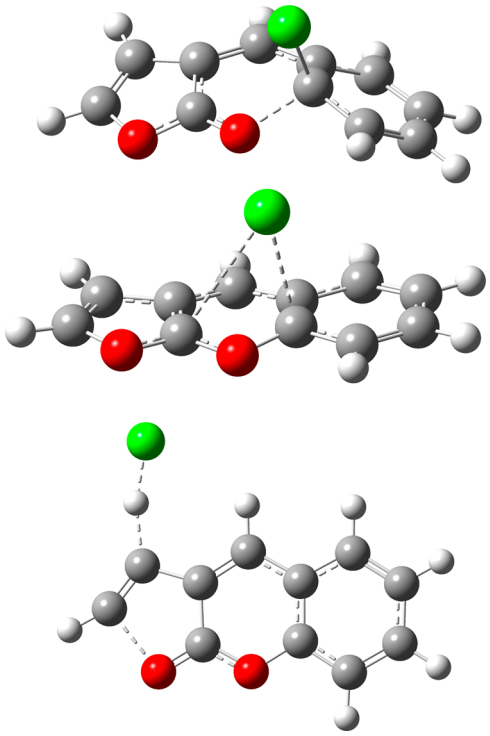


Figure 2. Transition states for the pathway shown in Scheme 5: (top) electrocyclization; (middle) 1,5-Cl migration; (bottom) HCl cleavage.

The key intermediate in the final two pathways is the enynol **22**. Its formation via two subsequent 1,3-hydrogen migrations (route c) can be discarded, as the direct 1,5-H shift (route d) has a significantly lower barrier (44 vs 74 kcal/mol). However, the last step (**22** → **20**) is problematic. The addition of alcohols to alkynes requires catalysis, traditionally by Hg(II) and a strong mineral acid; more recently, Au(III) catalysis has been reported.[9] The unassisted addition is unknown. In agreement with this, we estimate a very high energy of 83 kcal/mol for the potential zwitterion formed by a 5-*endo*-dig addition of the OH function in **22** to the alkyne with a fixed O−C distance of 1.35 Å; a minimum for such a structure was not found, even when a simulated solvent field was used. Alternatively, a 1,4-H shift in **22** leading to carbene **18** has a calculated barrier of 55 kcal/mol. Therefore, this reaction is not energetically competitive with route b.

The impact of *p*-nitro substitution of the phenyl ring (as used experimentally) on the reaction energies in route b starting from furanone **3e** was recalculated accordingly. It was found that the influence of the relatively remote position of the NO_2 group is negligible (less than 1 kcal/mol; see the Supporting Information for details), hence justifying the computations on unsubstituted compounds in Scheme 6.

CONCLUSION

FVT of 3-methylidenefuran-2(3*H*)-ones of types **1** and **3** yields allenyl ketones **2** and **4** by extrusion of CO. This reaction has a calculated free energy of activation of ca. 55 kcal/mol (Scheme 4). However, depending on substituents, different products may be formed. The formation of 3-ethynylcoumarin **6** from (*o*-halogenophenyl)methylidenefuranones requires *E*/*Z* isomerization of the methylidenefuranones (activation barrier ≈ 60 kcal/mol) followed by cyclization, halogen atom migration, and HX (X = Cl, Br) elimination (Schemes 1 and 5). This reaction has an overall calculated barrier of the order of ca. 50 kcal/mol after *E*/*Z* isomerization. Strongly electron-withdrawing substituents (nitroaryl or acetyl) on the allenes formed from arylmethylidenefuranones **7** and **11** and furyl- and thienylmethylidenefuranones **14** cause rearrangement to 2-arylfurans **10** and **13** and 2-furylfurans and 2-furylthiophenes **16** (Schemes 2, 3, and 6). Calculations indicate a readily accessible activation energy of the order of 40−45 kcal/mol for the cyclization via carbene **19** (Scheme 6).

EXPERIMENTAL SECTION

General. FVT reactions were carried out in unpacked quartz tubes (20 cm × 2 cm) using the apparatus and methodology described previously.[10] 3-(*o*-Chlorobenzylidene)-5-phenylfuran-2(3*H*)-one (**3a**) and 3-(*p*-nitrobenzylidene)-5-phenylfuran-2(3*H*)-one (**7a**) were prepared according to the literature method.[11]

3-(*o*-Bromobenzylidene)-5-phenylfuran-2(3*H*)-one (3b). A mixture of benzoylpropionic acid (7.12 g, 0.04 mol), *o*-bromobenzaldehyde (8.0 g, 0.04 mol), and anhydrous sodium acetate (4 g) in acetic anhydride (30 g) was heated at 100 °C under N_2 for 3 h. After cooling, the mixture was partially evaporated and then taken up in ethanol. The resulting solid was filtered, washed twice with hot water (100 mL each) and then with ice-cold ethanol, and recrystallized from ethanol to yield 7.7 g of **3b** (58% yield). Mp 159 °C; ^{1}H NMR ($CDCl_3$) δ 7.72 (m, 2H), 7.67 (m, 3H), 7.42 (m, 4H), 7.25 (m, 1H), 6.76 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 168.4, 157.8, 135.2, 133.6 (two signals), 131.0, 130.7, 130.0, 128.9, 127.8, 127.7, 127.5, 125.8, 125.4, 99.3; IR (KBr) 1770 (s), 1620 (m), 1610 (m), 1590 (m), 1570 (m), 1490 (m), 750 (s) cm^{-1}; MS *m*/*z* (%) 329 (M + 1, 3), 328 ($M^+(C_{17}H_{11}(^{81}Br)O_2)$, 16), 326 ($M^+(C_{17}H_{11}(^{79}Br)O_2)$, 18), 247 (81), 105 (100), 77 (63). Anal. Calcd for $C_{17}H_{11}BrO_2$: C, 62.24; H, 3.39. Found: C, 62.13, H, 3.40.

3-(Phenylethynyl)coumarin (6a). (a) A sample of 3-(*o*-chlorobenzylidene)-5-phenylfuran-2(3*H*)-one (**3a**) (500 mg, 1.8 mmol) was sublimed into the pyrolysis apparatus at 150 °C and thermolyzed at 750 °C and 10^{-3} hPa. The pyrolysate was isolated on a liquid N_2-cooled cold finger. After the end of the thermolysis, the cold finger was rinsed with a small amount of acetone. The acetone solution was used for the isolation of allene **4a** as described below. The remaining undissolved yellow solid was recrystallized from acetone to yield 180 mg of **6** (40% yield) as yellowish needles. Mp 176.5−177 °C (lit.[12] 176−177 °C); ^{1}H NMR ($CDCl_3$) δ 7.94 (m, 1H), 7.26−7.38 (m, 5H), 7.47−7.59 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 159.1, 133.0 (J_{CH} = 161.1 Hz), 144.6 (J_{CH} = 165.8 Hz), 131.9, 129.0, 128.3, 127.7 (J_{CH} = 164.1 Hz), 124.7 (J_{CH} = 164.3 Hz), 122.3, 132.0, 116.6 (J_{CH} = 166.9 Hz), 118.8, 153.3, 95.8, 83.3; IR (KBr) 3061 (vw), 2215 (vw), 1760,

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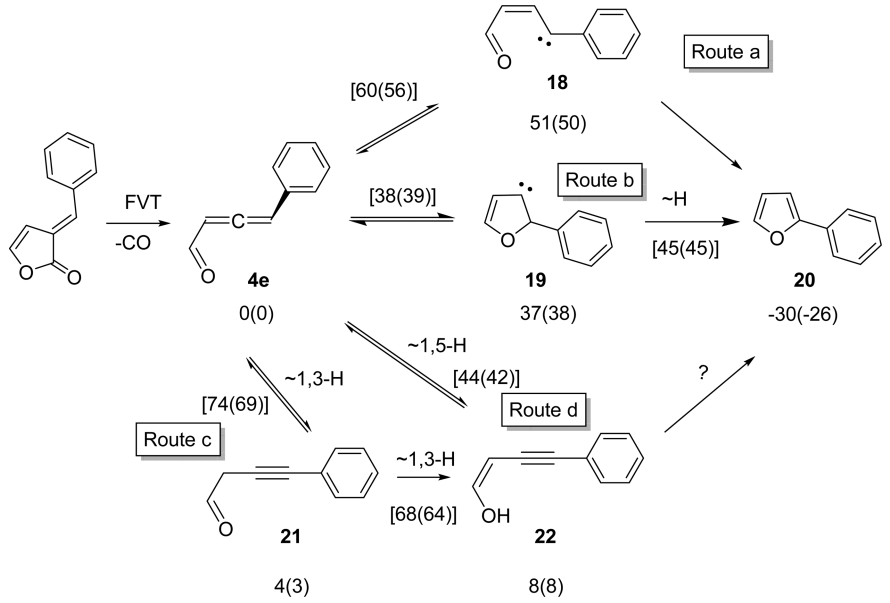
Scheme 6. Possible Routes from Allenyl Ketone 4e to 2-Phenylfuran (20)[a]



[a]Values of ΔE and (in parentheses) ΔG are in kcal/mol and were computed at the M06-2X/6-311+G(d,p) level. Values in brackets are transition state energies.

1724 (s), 1606, 1564, 1493, 1451, 1451, 1242, 1160, 1053, 927, 758, 689, 584, 528, 489 cm^{-1} (Figure S1 in the Supporting Information); Raman (solid) 3064, 2212 (vs), 1713 (vw), 1604 (s), 1563 (s), 1489, 1450, 1320, 1267, 1213, 1164, 1052, 996, 730, 448 cm^{-1} (Figure S2 in the Supporting Information); MS *m*/*z* (%) 248 (M + 2, 2), 247 (M + 1, 17), 246 (M^+, 100), 218 (47), 189 (35), 163 (6), 123 (5), 109 (8), 105 (4), 95 (15), 85 (5), 77 (9), 75 (15). Anal. Calcd for $C_{17}H_{10}O_2$: C, 82.91; H, 4.09. Found: C, 82.63; H, 4.09.

(b) 3-(*o*-Bromobenzylidene-5-phenylfuran-2(3*H*)-one (**3b**) (500 mg, 1.5 mmol) was subjected to FVT in the same way as described for **3a**, affording 190 mg of pure **6a** (48% yield) that was in every respect identical to the sample prepared from **3a**.

4-(*o*-Chlorophenyl)-1-phenylbuta-2,3-dienone (4a). The acetone solution from the aforementioned synthesis (a) of **6a** was subjected to preparative thin-layer chromatography on silica gel. Elution with toluene yielded 90 mg of **4a** (20% yield) as a yellow oil. ^1H NMR ($CDCl_3$) δ 7.92 (m, 2H), 7.49 (m, 5H), 7.21 (m, 2H), 7.10 (d, J = 6.4 Hz, 1H), 6.80 (d, J = 6.4 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 216.4, 190.2, 137.3, 133.0, 132.6, 129.9, 128.7, 129.4, 128.9, 128.8, 128.7, 128.4, 127.1, 97.3, 95.0; IR (film) 1940 (s), 1710 (m), 1655 (s), 1600 (s), 1575 (m), 1475 (s), 1450 (s), 1395 (m), 1275 (s), 1215 (s), 1050 (m), 1035 (m), 980 (m), 750 (s), 715 (m), 690 (m) cm^{-1}. Anal. Calcd for $C_{16}H_{11}OCl$: C, 75.43; H, 4.36. Found: C, 75.13; H, 4.33.

3-(*o*-Chlorobenzylidene-5-methylfuran-2(3*H*)-one (3c). A mixture of angelicalactone (9.8 g, 0.1 mol), *o*-chlorobenzaldehyde (14.1 g, 0.1 mol), and triethylamine (20 drops) was heated at 130 °C for 3 h. During this time, another 20 drops of triethylamine was added after 15 min and again after 1 h. The hot reaction mixture was added with stirring to 50 mL of $NaHSO_4$ solution. The resulting crystalline precipitate was dissolved in 1 L of ethanol, filtered, and then evaporated. The crystal mass was recrystallized from ethanol to yield 13.5 g of **3c** (61% yield). Mp 54.5−55 °C; ^1H NMR ($CDCl_3$) δ 7.60 (q, ^6J = 0.9 Hz, 1H), 7.55 (m, 1H), 7.45 (m, 1H), 7.30 (m, 2H), 6.15 (dq, ^4J = 1.3 Hz, ^4J = 0.8 Hz, 1H), 2.2 (dd, ^4J = 1.3 Hz, ^6J = 0.9 Hz, 3H, CH_3); ^{13}C NMR ($CDCl_3$) δ 168.9, 159.3, 135.3, 133.3, 130.6, 130.1 (d, J = 164 Hz), 129.7, 127.4, 126.9 (double peak), 101.6 (d, J = 178 Hz), 14.8 (q, J = 130 Hz); IR (KBr) 1760 (s), 1635 (m), 1610 (m), 1585 (m), 1470 (m), 1435 (m), 1180 (s), 1165 (s), 925 (s), 755 (s) cm^{-1}; MS *m*/*z* (%) 223 (M + 1, 1), 222 ($M^+(C_{12}H_9(^{37}Cl)O_2$, 10), 220 ($M^+(C_{12}H_9(^{35}Cl)O_2$, 3), 185 (43), 149 (8), 43 (100). Anal. Calcd for $C_{12}H_9ClO_2$: C, 65.32; H, 4.11. Found: C, 65.10; H, 4.10.

3-(*o*-Bromobenzylidene-5-methylfuran-2(3*H*)-one (3d). This compound was prepared from angelicalactone (4.3 g, 0.04 mol) and *o*-bromobenzaldehyde (7.98 g, 0.04 mol) in the same manner as described for **3c** above to yield 3.8 g of **3d** (36% yield) as light-yellow crystals. Mp 85.0−85.5 °C; ^1H NMR ($CDCl_3$) δ 7.63 (d, J = 7.3 Hz, 1H), 7.53 (d, J = 7.3 Hz, 1H), 7.52 (s, 1H), 7.35 (t, J = 7.3 Hz, 1H), 7.21 (t, J = 7.3 Hz, 1H), 6.12 (s, 1H), 2.17 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 168.3, 159.0, 134.3, 132.5, 131.3, 130.5, 129.4, 127.3, 126.9, 125.1, 101.2, 14.9; IR 1760 (s), 1625 (s), 1600 (m), 1575 (m), 1420 (s), 1380 (s), 1370 (s), 1165 (s), 1020 (s), 910 (s), 740 (s) cm^{-1}; MS *m*/*z* (%) 266 ($M^+(C_{12}H_9(^{81}Br)O_2$, 7), 264 ($M^+(C_{12}H_9(^{79}Br)O_2$, 7), 185 (68), 114 (21), 43 (100). Anal. Calcd for $C_{12}H_9BrO_2$: C, 54.37; H, 3.42. Found: C, 54.49; H, 3.29.

3-(1-Propynyl)coumarin (6b). (a) A sample of **3c** (1 g, 4.7 mmol) was sublimed at 90 °C and thermolyzed at 750 °C and 5 × 10^{-4} hPa. The resulting product was collected on a liquid nitrogen-cooled cold finger and featured a medium absorption at 1938 cm^{-1} in the IR spectrum. The product was taken up in acetone and subjected to preparative thin-layer chromatography (silica gel/toluene), which afforded a slightly yellow and strongly blue-fluorescing material. Sublimation of this material afforded 440 mg of **3c** (52% yield) as a nearly white product. Mp 120.5−121 °C; ^1H NMR ($CDCl_3$) δ 7.78 (s, 1H), 7.48 (dd, J = 7.2, 8.3 Hz, 1H), 7.42 (d, J = 7.8 Hz, 1H), 7.29 (d, J = 8.3 Hz, 1H), 7.25 (dd, J = 7.2, 7.8 Hz, 1H), 2.1 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 159.8, 153.1, 144.1 (J_{CH} = 165.6 Hz), 131.7 (J_{CH} = 152.3 Hz), 127.4 (J_{CH} = 163.6 Hz), 124.6 (J_{CH} = 162.2 Hz), 118.9, 116.6 (J_{CH} = 164.8 Hz), 113.6, 93.6, 4.7; IR (KBr) 3040 (w), 2915 (w), 2220 (w), 1722 (s), 1610 (m), 1450 (m), 1100 (s), 645 (s) cm^{-1}; Raman (solid) 2220 (s), 1610 (vs), 1556 (s), 1100 (s) cm^{-1}; MS *m*/*z* 185 (M + 1, 13), 184 (M^+, 100), 156 (18), 155 (26), 128 (23), 127 (12), 102 (16), 77 (8), 75 (8), 64 (10), 63 (17), 51 (18). Anal. Calcd for $C_{12}H_8O_2$: C, 78.25; H, 4.38. Found: C, 78.08; H, 4.28.

(b) *o*-Bromobenzylidenefuranone **3d** (500 mg, 1.8 mmol) was subjected to FVT in the same manner as described for the chloro derivative **3c** above. The crude product exhibited a weak allene peak at 1935 cm^{-1} in the IR spectrum. Workup as described above yielded 220 mg of pure **6b** (64% yield).

2-(*p*-Nitrophenyl)-5-phenylfuran (10a). FVT of 3-(*p*-nitrobenzylidene)-5-phenylfuran-2(3*H*)-one (**7a**) (500 mg, 1.7 mmol) at 750 °C afforded a product exhibiting a characteristic allene peak at 1937 cm^{-1}; however, the allene peak disappeared in the course of 45 min at RT. Chromatographic workup as described above afforded 317

dx.doi.org/10.1021/jo402139a | J. Org. Chem. 2014, 79, 65−71

mg of **10a** (70% yield). Mp 134−135 °C; ^{1}H NMR ($CDCl_3$) δ 8.26 (d, 2H), 7.84 (d, 2H), 7.76 (d, 2H), 7.41 (t, 2H), 7.33 (t, 1H), 6.96 (d, J = 3.6 Hz, 1H), 6.80 (d, J = 3.6 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 155.7, 151.0, 146.4, 136.3, 130.0, 128.8, 128.3, 124.4, 124.2, 123.7, 111.3, 107.8; the ^{1}H and ^{13}C NMR spectra are in accord with literature data;[13] MS m/z (%) 266 (M + 1, 10), 265 (M^+, 100), 237 (44), 119 (26), 189 (37), 161 (89), 139 (100), 83 (61), 59 (61).

3-(*m*-Nitrobenzylidene)-5-phenylfuran-2(3*H*)-one (7b). This compound was prepared from benzoylpropionic acid (8.8 g, 0.05 mol) and *m*-nitrobenzaldehyde (15.1 g, 0.05 mol) in the manner described above for **3b** to yield 9.5 g of **7b** (69% yield). Mp 209 °C; ^{1}H NMR (acetone-d_6) δ 8.58 (broad s, 1H), 8.36 (fd, J = 8 Hz, 1H), 8.28 (m, 1H), 7.92 (m, 1H), 7.80 (t, J = 8 Hz, 2H), 7.55 (m, 4H), 7.66 (d, J = 0.8 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 178.1, 159.0, 136.8, 135.5, 131.4, 131.3, 130.2 (two signals), 129.0, 128.0, 127.6, 125.8, 124.2, 123.8, 99.0; IR (KBr) 1765 (s), 1755 (s), 1565 (m), 1520 (s), 1490 (m), 1350 (s), 785 (s) cm^{-1}; MS m/z (%) 293 (M^+, 37), 119 (53), 105 (100), 92 (24), 77 (82). Anal. Calcd for $C_{17}H_{11}NO_4$: C, 69.62; H, 3.78; N, 4.78. Found: C, 69.76; H, 3.62; N, 4.73.

2-(*m*-Nitrophenyl)-5-phenylfuran (10b). The product of FVT of 3-(*m*-nitrobenzylidene)-5-phenylfuran-2(3*H*)-one (**7b**) (500 mg, 1.7 mmol) at 750 °C showed a characteristic allene absorption an 1938 cm^{-1}, but this compound was not isolable in substance. Chromatographic workup as described above afforded 320 mg of **10b** (71% yield) as a viscous oil. ^{1}H NMR ($CDCl_3$) δ 8.53 (m, 1H), 8.08 (m, 1H), 8.00 (m, 1H), 7.76 (t, 1H), 7.55 (t, 1H), 7.43 (t, 2H), 7.31 (m, 2H), 6.78 (d, J = 3.5 Hz, 1H), 6.89 (d, J = 3.5 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 154.7, 150.7, 148.8, 132.2, 130.1, 129.7, 129.0, 128.8, 128.0, 124.0, 121.5, 119.2, 109.5, 107.4. The ^{1}H and ^{13}C NMR data are in accord with literature data.[14]

4-Acetyl-5-methyl-3-(*p*-methoxybenzylidene)furan-2(3*H*)-one (11). A mixture of levulinic acid (6 g, 0.05 mol), *p*-methoxybenzaldehyde (6 g, 0.06 mol), and anhydrous sodium acetate (4 g) in acetic anhydride (20 g) was heated under N_2 at 100 °C for 3 h. After cooling in ice, the mixture was filtered, and the solid was suspended in water and extracted with diethyl ether. Crystallization of the condensed ether extract yielded 2.1 g of **11** (16% yield) as intensely yellow crystals. Mp 136.5−137 °C; ^{1}H NMR ($CDCl_3$) δ 8.28 (s, 1H), 8.10 (d, J = 9.0 Hz, 2H), 6.93 (d, J = 9.0 Hz, 2H), 3.83 (s, 3H), 2.49 (s, 3H), 2.47 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 193.4, 164.3, 161.8, 160.8, 144.9, 134.4, 126.7, 118.0, 113.6, 55.2, 31.4, 15.9; IR (KBr) 1760 (s), 1660 (s), 1615 (s), 1255 (s), 1380 (s), 950 (s) cm^{-1}; MS m/z (%) 260 (M + 2, 23), 259 (M + 1, 15), 258 (M^+, 100), 188 (89), 145 (27), 43 (50). Anal. Calcd for $C_{15}H_{14}O_4$: C, 69.79; H, 5.47. Found: C, 69.97; H, 5.43.

3-Acetyl-5-(*p*-methoxyphenyl)-2-methylfuran (13). The foregoing compound **11** (100 mg, 0.4 mmol) was subjected to FVT at 720 °C. The resulting product was recrystallized from petroleum ether to yield 18 mg of **13** (20% yield). ^{1}H NMR ($CDCl_3$) δ 7.57 (d, J = 8.9 Hz, 2H), 6.92 (d, J = 8.9 Hz, 2H), 6.71 (s, 1H). The ^{1}H NMR spectrum was identical with spectra reported in the literature.[15]

4-Acetyl-3-furfurylidene-5-methylfuran-2(3*H*)-one (14a). A mixture of levulinic acid (11.3 g, 0.1 mol), 2-furaldehyde (9.6 g, 0.1 mol), and anhydrous sodium acetate (8.2 g) in acetic anhydride (60 g) was heated under N_2 at 100 °C for 3 h. The cooled mixture was filtered, and the solid was washed twice with water and then recrystallized from ethanol to yield 6.1 g of **14a** (28% yield). Mp 177 °C; ^{1}H NMR ($CDCl_3$) δ 8.28 (s, 1H), 8.13 (d, J = 3.7 Hz, 1H), 7.61 (d, J = 1.5 Hz, 1H), 6.60 (m, 1H), 2.53 (s, 3H), 2.47 (s, 3H). ^{13}C NMR ($CDCl_3$) δ 193.0, 164.1, 161.4, 151.3, 146.2, 128.9, 120.5, 117.5, 116.5, 113.7, 31.3, 16.0. Anal. Calcd for $C_{12}H_{10}O_4$: C, 66.05; H, 4.62. Found: C, 66.10; H, 4.61.

2-(4-Acetyl-5-methylfuran-2-yl)furan (16a). 4-Acetyl-3-furfurylidene-5-methylfuran-2(3*H*)-one (**14a**) (500 mg, 2.3 mmol) was subjected to FVT at 720 °C. The resulting yellow solid was recrystallized from petroleum ether to yield 330 mg of **16a** (78% yield) as light-yellow crystals. Mp 51.0−51.5 °C; ^{1}H NMR ($CDCl_3$) δ 7.41 (dd, J = 1.9, 0.7 Hz, 1H), 6.73 (s, 1H), 6.55 (d, J = 3.4 Hz, 1H), 6.45 (dd, J = 3.4, 1.9 Hz, 1H), 2.63 (s, 3H), 2.43 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 193.7, 157.4, 145.3, 144.1, 141.9, 122.5, 111.2, 105.5, 104.9, 28.8, 14.1; IR (KBr) 1660 (s), 1570 (s), 1535 (m), 1405 (s), 1215 (s), 1010 (s), 950 (s), 885 (s) cm^{-1}; MS m/z (%) 191 (M + 1, 11), 190 (M^+, 100), 175 (62), 43 (52). Anal. Calcd for $C_{11}H_{10}O_3$: C, 69.47; H, 5.30. Found: C, 69.37; H, 5.18.

4-Acetyl-5-methyl-3-thienylidenefuran-2(3*H*)-one (14b). This compound was prepared from 2-thiophenaldehyde (8.9 g, 0.1 mol) and levulinic acid in the same manner as described above for **14a** to yield 6.1 g of **14b** (23% yield). Mp 179−180 °C; ^{1}H NMR ($CDCl_3$) δ 8.60 (d, J = 0.6 Hz, 1H), 7.80 (d, J = 3.8 Hz, 1H), 7.67 (d, J = 5.0 Hz, 1H), 7.15 (dd, J = 3.8, 5.0 Hz, 1H), 2.53 (s, 3H), 2.48 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 193.4, 164.5, 161.1, 138.4, 137.9, 135.9, 134.6, 127.6, 117.5, 116.4, 31.5, 16.1; IR (KBr) 1765 (s), 1640 (s), 1600 (s), 1390 (s), 935 (s) cm^{-1}; MS m/z (%) 236 (M^+($C_{12}H_{10}O_3$(^{34}S)), 5), 235 (M^+($C_{12}H_{10}O_3$(^{32}S)) + 1, 13), 234 (M^+($C_{12}H_{10}O_3$(^{32}S)), 96), 218 (2), 164 (92), 121 (25), 43 (100). Anal. Calcd for $C_{12}H_{10}O_3S$: C, 61.52; H, 4.30. Found: C, 61.45; H, 4.29.

2-(4-Acetyl-5-methylfuran-2-yl)thiophene (16b). This compound was prepared by FVT of 4-acetyl-5-methyl-3-thienylidenefuran-2(3*H*)-one (**14b**) (300 mg, 1.3 mmol) in the same manner as described above for **16a** to yield 210 mg of **16b** (79% yield). Mp 62.0−62.5 °C; ^{1}H NMR (DMSO-d_6) δ 7.55 (dd, J = 5.0, 1.1 Hz, 1H), 7.38 (dd, J = 3.6, 1.1 Hz, 1H), 7.12 (dd, J = 5.0, 1.1 Hz, 1H), 7.09 (s, 1H), 2.57 (s, 3H), 2.41 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 193.7, 157.4, 147.1, 132.5, 124.5, 127.6, 123.0 (two signals), 104.9, 29.0, 14.3; IR (KBr) 1670 (s), 1590 (m), 1560 (s), 945 (s), 840 (s), 700 (s) cm^{-1}; MS m/z (%) 208 (M + 2, 5%), 207 (M + 1, 13), 206 (M^+, 100), 191 (63), 163 (32), 121 (17), 43 (40). Anal. Calcd for $C_{11}H_{10}O_2S$: C, 64.06; H, 4.89. Found: C, 64.35; H, 4.52.

COMPUTATIONAL SECTION

All of the calculations were performed with the Gaussian 09 program package.[16] Structures were optimized using the global hybrid functionals M06-2X[17] and B3LYP[18] as well as the range-separated hybrid functional ωB97X-D[19] with the 6-311+G(d,p) basis set.[20] The nature of each stationary point as a true minimum or a first-order transition state was confirmed by calculating harmonic frequencies. Gibbs free energies were obtained at 298.15 K under inclusion of scaled zero-point vibrational energy corrections.[21] The wave function stabilities of selected transition states and their open-shell characters were examined; however, no instability or diradical character could be found, except for **18**, where the triplet species is more stable by 8 kcal/mol. However, the reaction clearly proceeds via the singlet carbene. The effect of a solvent field was not evaluated, as most of the reactions reported herein take place under gas-phase conditions.

ASSOCIATED CONTENT

Supporting Information

Experimental and calculated IR and Raman spectra of **6a**, absolute energies for all calculated compounds, comparison of computational methods, and calculated equilibrium geometries of ground and transition states with imaginary frequencies for the latter. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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