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A Platinum Complex-Catalyzed Reaction of 3-Chloro-1,3-diene Monoepoxides with Carbon Nucleophiles Involving Nucleophilic Substitution at the Central Carbon Atom of the π-Allyl Ligand in the Intermediate Complex. Dependency of Regioselectivity upon the Added Lewis Acids

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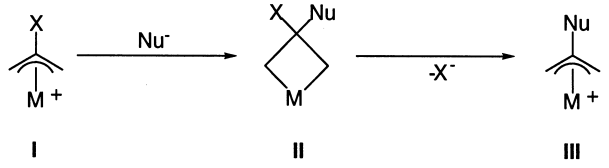
Abstract—The reaction of 3-chloro-1,3-diene monoepoxides with sodium ethyl acetoacetate in the presence of a catalytic amount of platinum(0) complex resulted in the formation of furan derivatives. The key feature of this new platinum-catalyzed reaction is the nucleophilic substitution at the central carbon atom of the (π-allyl) complexes, which are formed as intermediates. Then cyclization follows to give furans. Different regio isomers were obtained by changing the Lewis acid added.

Introduction

The reactions of (π-allyl) transition metal complexes with nucleophiles has been the subject of extensive investigations and has led to a number of synthetically useful methods for the introduction of three carbon units into organic compounds. In this area, however, the major effort has been directed at allylation, via nucleophilic attack at the terminal carbon atom of (π-allyl) complexes.[1] The recent report of a nucleophilic attack at the central carbon atom of π-allyl complexes, although rare, has attracted attention.[2,3] It is noteworthy that we previously reported on the first example of nucleophilic substitution at the central carbon atom of (π-allyl) complex.[4] For example, in the presence of $Pt(C_2H_4)(PPh_3)_2$ the reaction of 2-chloroallyl acetate with sodium diethyl methylmalonate gave the doubly alkylated product, and with sodium ethyl acetoacetate it resulted in a furan derivative. These reactions proceed via a nucleophilic attack at the central carbon atom of a (π-allyl) complex (I), followed by the elimination of X^- from the metallacyclobutane (II) to give the (π-allyl) complex (III), substituted at the central carbon atom (in Scheme 1).



Scheme 1.

Only a limited number of examples of this type of reaction have been reported thus far.[5] We carried out further studies on this new process and wish to report some of these findings here. The use of 3-chloro-1,3-diene monoepoxides, instead of 2-chloroallyl acetate as a substrate appeared promising. In the common method of allylic alkylation, it is known that (π-allyl) transition metal complexes are generated from 1,3-diene monoepoxides and that these react with protonated nucleophiles, because the alkoxide which is produced as the result of epoxide ring opening, functions as a base[6] (Scheme 2).

In this paper, we report the platinum-catalyzed reaction of 3-chloro-1,3-diene monoepoxides with carbon nucleophiles. In this case, nucleophilic substitution at the central carbon atom of (π-allyl) complexes did take place. The regioselectivity of the ring closure in the subsequent step is altered by the nature of the Lewis acid added.

Results and Discussion

The reaction of 3-chloro-1,3-diene monoepoxide with a carbon nucleophile, carrying an acetyl group would be expected to proceed according to the sequence shown in Scheme 3.

Keywords: platinum and compounds; catalysts; substitution.
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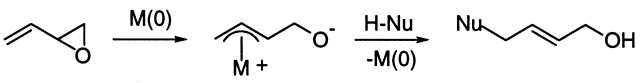
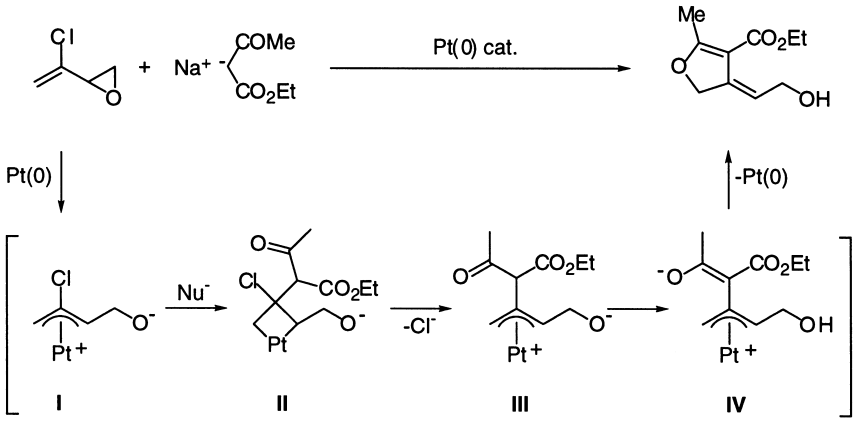


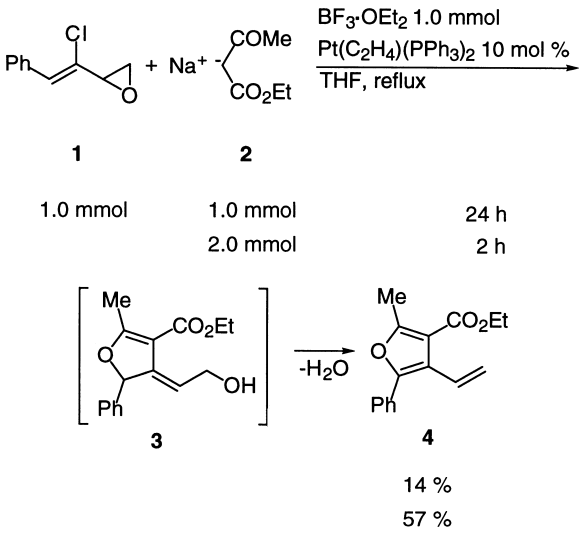
Scheme 2.



Scheme 3.

This reaction involves three important processes: (1) formation of an (π-allyl) complex from 3-chloro-1,3-diene monoepoxide (to I); (2) a nucleophilic substitution at the central carbon atom of the (π-allyl) complex (I to III); and (3) an enolate oxygen cyclization (IV to product).

The platinum-catalyzed reaction of 3-chloro-4-phenyl-1,3-diene monoepoxide **1** with carbon nucleophile was initially carried out. The reaction of **1** (1.0 mmol) with sodium ethyl acetoacetate **2** (1.0 mmol) in the presence of $Pt(C_2H_4)(PPh_3)_2$ (0.1 mmol) as catalyst was investigated, but resulted in no reaction. It appears that the epoxide ring of **1** is not opened by the platinum(0) catalyst, or, that it returns to the starting epoxide immediately from the intermediate formed (π-allyl) platinum complex. In order to activate the epoxide ring towards ring opening, a Lewis acid was then added. The use of $BF_3{\cdot}OEt_2$ was effective in this case. The reaction of 3-chloro-1,3-diene monoepoxide **1** (1.0 mmol) with sodium ethyl acetoacetate **2** (1.0 mmol) in the presence of $Pt(C_2H_4)(PPh_3)_2$ (0.1 mmol) and $BF_3{\cdot}OEt_2$ (1.0 mmol) in THF at reflux gave the furan derivative **4** in 14% yield as the result of a nucleophilic substitution at the central carbon (Eq. 1).



(1)

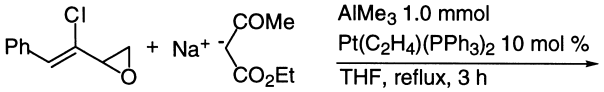
Table 1. Variation of Lewis acids

Entry	Lewis acid (mmol)	Temp.	Time (h)	Product	Yield (%)
1	$BF_3{\cdot}OEt_2$ (1.0)	Reflux	2	**4**	57
2	$BF_3{\cdot}OEt_2$ (0.1)	Reflux	1	Complicated	
3	$BF_3{\cdot}OEt_2$ (1.0)	R.t.	24	**4**	26[a]
4	$AlMe_3$ (1.0)	Reflux	3	**5**	87
5	$AlMe_3$ (0.1)	Reflux	24	No reaction	
6	$AlMe_3$ (1.0)	R.t.	27	**5**	74
7	$AlMe_2Cl$ (1.0)	Reflux	6	**5**	31
8	$AlEt_3$ (1.0)	Reflux	2	**5**	85
9	$AlEt_2Cl$ (1.0)	Reflux	6	**5**	50
10	$AlEt_2(Oet)$ (1.0)	Reflux	22	**5**	17

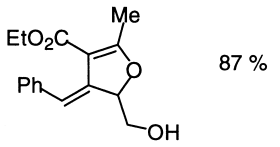
[a] 1,3-Diene monoepoxide was not consumed completely.

This reaction must have proceeded in the manner shown in Scheme 3. The dehydration of **3** followed by *exo* to *endo* double-bond isomerization would be predicted to give the product **4**. While **4** was, in fact, formed, the yield was very low and the starting monoepoxide **1** was not completely consumed. This reaction was then carried out using 2 equiv. of sodium ethyl acetoacetate **2** (1 equiv. excess as the base), and a satisfactory result was obtained with **4** in a yield of 57%. It is interesting that the boron compound activated the epoxide in the presence of an excess of the base. We next examined other Lewis acids. Interestingly, when $AlMe_3$ was used as a Lewis acid, dihydrofuran **5** was obtained in 87% yield (Eq. 2). The regioselectivity of enolate oxygen cyclization leading to **5** was the inverse of

from that for **3** (vide infra).

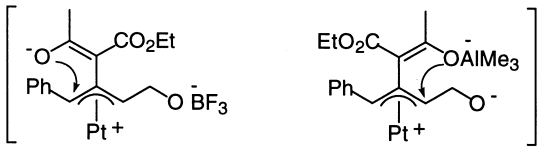


1 1.0 mmol — **2** 2.0 mmol (2)



5 87 %

The effect of the amount of Lewis acid and the reaction temperature was examined for the reaction of 3-chloro-1,3-diene monoepoxide **1** with sodium ethyl acetoacetate **2** (entries 1–6, Table 1). In the case of $BF_3{\cdot}OEt_2$, the reaction using a catalytic amount of the Lewis acid was complicated (entry 2), and, when run at room temperature resulted in a low yield (entry 3). Also in the case of $AlMe_3$, the reaction required a stoichiometric amount of $AlMe_3$ and proceeded smoothly at reflux temperature (entries 4–6). Other Lewis acids were also investigated (entries 7–10, Table 1). The use of $AlEt_3$ resulted in a high yield (entry 8), but aluminium compounds having an electronegative group were only moderately effective (entries 7, 9 and 10). No reaction was observed when BCl_3 $AlCl_3$, $TiCl_4$, $Ti(OiPr)_4$, $TiCl(OiPr)_3$, $FeCl_3$ or $ZnEt_2$, were used.



A **B**

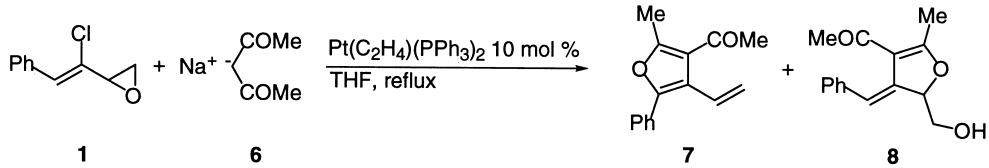
The difference in the regiochemistry, as caused by differences in the Lewis acid used may be explained, as follows. Two different types of coordination of the Lewis acid to the (π-allyl) intermediate are possible (intermediate **A** and **B**).

When $BF_3{\cdot}OEt_2$ was used, intermediate **A** is formed, and the use of $AlMe_3$ resulted in intermediate **B**. In **A**, boron appears to attach the epoxide oxygen atom, and the enolate oxygen anion would attack the terminal carbon atom carrying the phenyl group in the π-allyl ligand because phenyl group aids in stabilizing the partial positive charge. In the case of **B**, aluminium forms an ate complex with the enolate oxygen anion and, therefore, the enolate oxygen anion would tend to attack the terminal carbon atom carrying hydroxymethyl group because of smaller steric hindrance.

Sodium acetylacetonate **6**, as a carbon nucleophile, behaved in a similar manner, although the yield was low when $AlMe_3$ was used and the substrate was not consumed completely in 1 h (Eq. 3). Longer reaction times led to even lower yields due to product decomposition.

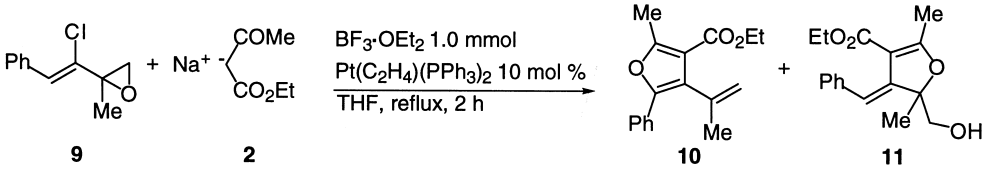
A carbon nucleophile which contains no acetyl group, such as sodium diethyl malonate, did not react with 3-chloro-1,3-diene monoepoxide. That the nucleophilic substitution at the central carbon atom of (π-allyl) complex is sensitive to the nature of nucleophiles was also observed in the case of 2-chloroallyl acetate,[4] and the use of sodium diethyl malonate as the nucleophile resulted in no reaction. In either case, the lack of reaction appears to be due to the formation of stable trimethylenemethane–platinum complexes through nucleophilic substitution at the central carbon atom of the π-allyl ligands, followed by deprotonation.[7]

The 3-chloro-2-methyl-4-phenyl-1,3-diene monoepoxide **9**, which contains a methyl group at the 2-position was then used as a substrate with the expectation that ring opening of



1 1.0 mmol — **6** 2.0 mmol — **7** — **8** (3)

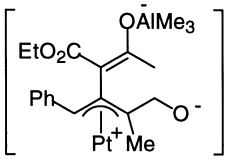
no additive	24 h	no reaction	
$BF_3{\cdot}OEt_2$ (1.0 mmol)	4 h	69 %	0 %
$AlMe_3$ (1.0 mmol)	1 h	0 %	29 %



9 1.0 mmol — **2** 2.0 mmol — **10** 20 % — **11** 36 % (4)

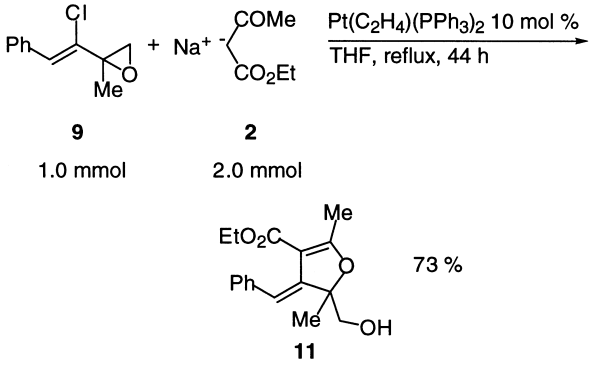
the epoxide would take place easier. In the presence of $BF_3{\cdot}OEt_2$, the reaction of 3-chloro-1,3-diene monoepoxide **9** with sodium ethyl acetoacetate **2** gave, not only furan **10**, but also dihydrofuran **11**, in 20 and 36% yield, respectively (Eq. 4). The formation of **11** indicates that the stabilization of the positive charge for enolate cyclization is also assisted by the methyl group.

The use of $AlMe_3$ (1.0 mmol) instead of $BF_3{\cdot}OEt_2$ resulted in no reaction. This suggests that the bulky ate complex of the enolate oxygen anion with $AlMe_3$ does not attack either at the terminal carbon atoms in intermediate **C**.



C

Interestingly, this 1,3-diene monoepoxide **9** reacted with sodium ethyl acetoacetate **2** in the presence of $Pt(C_2H_4)(PPh_3)_2$ to give dihydrofuran **11** as the sole product in 73% yield without the use of a Lewis acid (Eq. 5). This result can be attributed to the easier ring opening of epoxide **9** in the presence of the methyl group.



(5)

Conclusion

A new platinum(0)-catalyzed reaction is described. The ring opening of 3-chloro-1,3-diene monoepoxides by Pt(0) provides access to a (π-allyl) transition metal complex in which the leaving group exists at the central carbon atom of the π-allyl ligand. An appropriate carbon nucleophile can then undergo nucleophilic substitution at the central carbon atom of the (π-allyl) complex. It has been found that the added Lewis acids play important roles especially in regio selection in the product-determining cyclization step. Our findings point to the possibility that boron may attach the epoxide oxygen during the reaction process, and that aluminium might not attach to the epoxide oxygen but, rather, to the enolate oxygen anion.

Experimental

General information

Boiling points (bp) refer to air bath temperatures for bulb-to-bulb distillation and are uncorrected. ^{1}H NMR and ^{13}C NMR were recorded on a JEOL JMN-270 spectrometer in $CDCl_3$ using tetramethylsilane as an internal standard. Data are reported as follows: chemical shifts in ppm (δ), multiplicity (s=singlet, d=doublet, t=triplet, q=quartet, qui=quintet, and m=multiplet), coupling constant (Hz), integration, and interpretation. Infrared spectra (IR) were obtained on a Hitachi 270-50 spectrometer; absorption maxima are reported in reciprocal centimeters with the following relative intensities: s (strong), m (medium), or w (weak). Mass spectra were obtained on a Shimadzu GCMS-QP 5000 instrument using an ionization voltage of 70 eV. Elemental analyses were performed by the Elemental Analysis Section of Osaka University. High-resolution mass spectra (HRMS) were obtained on a JEOL JMS-DX303. Analytical GC was carried out on a Shimadzu GC-12A gas chromatography, equipped with a flame ionization detector. Column chromatography was performed with SiO_2 (MERCK). THF was distilled over Na-benzophenone prior to use. $Pt(C_2H_4)(PPh_3)_2$[9] was prepared according to published procedures.

Preparation of 3-chloro-1,3-diene monoepoxides

3-Chloro-1,3-diene monoepoxides **1** and **9** were prepared by Corey–Chaykovsky epoxidation.[10]

3-Chloro-4-phenyl-1,3-diene monoepoxide (1). A solution of methylsulfinyl carbanion was prepared in the usual manner, under nitrogen, from sodium hydride (2.16 g, 90 mmol) and dry dimethyl sulfoxide (60 mL) at 80°C. After cooling to room temperature, the solution was diluted with dry THF (60 mL), and then cooled in a salt–ice bath (below 0°C). A solution of trimethylsulfonium iodide (18.36 g, 90 mmol) in dimethyl sulfoxide (60 mL) was added, dropwise over a 20 min period. After the addition of the salt was complete, a solution of α-chloro-cinnamaldehyde (12.50 g, 75 mmol) in THF (30 mL) was immediately added. Stirring was continued below 0°C for 1 h and then for 1 h at room temperature. The reaction mixture was diluted with water (300 mL) and the resulting solution was extracted with diethyl ether, and the combined organic layer was then dried over $MgSO_4$. The ether was evaporated and the residue was purified by column chromatography on silica gel (eluent; hexane/ethyl acetate=10:1) to give a slightly yellow liquid (7.71 g, 43 mmol, 57% yield). R_f 0.23 (hexane/ethyl acetate=10:1). ^{1}H NMR ($CDCl_3$): δ 2.96–3.03 (m, 2H, CH_2), 3.66 (dd, J=3.6 Hz, J=2.6 Hz, 1H, CH), 6.87 (s, 1H, CH), 7.27–7.41 (m, 3H, *m*,*p*-Ph), 7.64–7.67 (m, 2H, *o*-Ph). ^{13}C NMR ($CDCl_3$): δ 47.7 (1-C), 54.3 (2-C), 127.0 (4-C), 128.3 (*m*-ph), 128.4 (*p*-ph), 129.2 (*ipso*-ph), 129.3 (*o*-ph), 133.9 (3-C). IR (neat): 3064m, 3032m, 3000m, 2920 w, 1956 w, 1894 w, 1810 w, 1762 w, 1644 m, 1600 w, 1580 w, 1496 s, 1474 w, 1452 s, 1390 m, 1338 w, 1308 w, 1284 m, 1254 m, 1206 w, 1182 w, 1158 m, 1136 m, 1122 m, 1090 m, 1074 m, 1030 w, 1000 w, 958 s, 920 m, 870 s, 828 s, 784 m, 756 s, 692 s, 670 m, 612 m, 576 m, 544 w, 514 m, 450 w cm^{-1}. MS (70 eV):

m/z (relative intensity, %) 182 (M^++2, 3), 181 (M^++1, 2), 180 (M^+, 11), 145 (17), 127 (11), 117 (13), 116 (16), 115 (100), 89 (13), 63 (18), 51 (18), 50 (13). Found: C 66.67; H 5.05; Cl 19.73. Anal. Calcd for $C_{10}H_9OCl$: C 66.49; H 5.02; O 8.86; Cl 19.63. HRMS Found: 180.0346. Calcd for $C_{10}H_9OCl$: 180.0342.

3-Chloro-1-methyl-4-phenyl-1,3-diene monoepoxide (9). To the Grignard reagent MeMgI [prepared in situ from Mg (2.92 g, 120 mmol) and iodomethane (17.03 g, 120 mmol)] in diethyl ether (180 mL) at room temperature was added a diethyl ether solution (30 mL) of α-chlorocinnamaldehyde (13.33 g, 80 mmol). The mixture was stirred for 12 h, and a saturated aqueous solution (180 mL) of NH_4Cl was added, followed by extraction with diethyl ether. The combined organic layer was dried over $MgSO_4$, and concentrated in vacuo. The residue was distilled under reduced pressure, to give 3-chloro-4-phenyl-3-buten-2-ol (bp 76–80°C/1 mmHg, 14.22 g, 78 mmol). This alcohol was oxidized with pyridinium chlorochromate (23.70 g, 110 mmol) in CH_2Cl_2 (200 mL) to give 3-chloro-4-phenyl-3-buten-2-one, which was purified by column chromatography (R_f 0.20, eluent; hexane/ethyl acetate=10:1, 11.20 g, 62 mmol). The resulting ketone was epoxidated in the same manner as described for **1** to give a slightly yellow liquid, in an overall yield of 30% (4.69 g, 24 mmol). R_f 0.33 (hexane/ethyl acetate=10:1). ^{1}H NMR ($CDCl_3$): δ 1.66 (s, 3H, CH_3), 2.85 (d, *J*=5.5 Hz, 1H, one proton of CH_2), 2.97 (d, *J*=5.5 Hz, 1H, one proton of CH_2), 6.85 (s, 1H, CH), 7.28–7.39 (m, 3H, *m*,*p*-Ph), 7.61–7.64 (m, 2H, *o*-Ph). ^{13}C NMR ($CDCl_3$): δ 20.3 (CH_3), 55.6 (1-C), 58.8 (2-C), 124.3 (4-C), 128.1 (*p*-ph), 128.2 (*m*-ph), 128.6 (*ipso*-ph), 129.2 (*o*-Ph), 134.1 (3-C). IR (neat): 3060 m, 3032 w, 2992 m, 2936 w, 2288 w, 1954 w, 1890 w, 1808 w, 1760 w, 1722 w, 1672 w, 1648 w, 1602 w, 1580 w, 1498 s, 1450 s, 1384 m, 1346 m, 1262 s, 1198 m, 1144 w, 1108 w, 1076 s, 1008 m, 968 s, 916 m, 868 s, 850 s, 820 s, 756 s, 694 s, 668 s, 610 w, 582 m, 516 m, 496 w, 444 w, 406 w, 366 w cm^{-1}. MS (70 eV): *m/z* (relative intensity, %) 196 (M^++2, 5), 194 (M^+, 16), 167 (10), 165 (32), 159 (24), 158 (50), 130 (20), 129 (100), 128 (58), 127 (32), 115 (26), 77 (13), 51 (13). Found: C 68.00; H 5.80; Cl 17.96. Anal. Calcd for $C_{11}H_{11}OCl$: C 67.87; H 5.70; O 8.22; Cl 18.21.

Typical procedure. The platinum-catalyzed reaction of 3-chloro-1,3-diene monoepoxide with carbon nucleophile

Ethyl acetoacetate (260 mg, 2.0 mmol) was added to a suspension of NaH (60 wt% in mineral oil, 80 mg, 2.0 mmol) in THF (10 mL) at 0°C. The mixture was stirred at room temperature for 30 min at which time $Pt(C_2H_4)(PPh_3)_2$ (74.7 mg, 0.1 mmol) was added. 3-Chloro-1,3-diene monoepoxide **1** (180.0 mg, 1.0 mmol) and $BF_3{\cdot}OEt_2$ (0.13 mL, 1.0 mmol) were added, and the flask was then immersed in an oil bath at 80°C. The reaction was monitored by analytical GC, and, after 2 h the substrate had been completely consumed. After the reaction mixture was cooled to room temperature, water (10 mL) was added. The resulting solution was extracted with diethyl ether, and the combined organic layer was dried over $MgSO_4$, and concentrated in vacuo to give yellow oil. The residue was subjected to purification by kugelrohr distillation to give ethyl 2-methyl-5-phenyl-4-vinylfuran-3-carboxylate **4** (bp 140–170°C/1 mmHg, 145 mg, 57% yield) as a yellow liquid.

Ethyl 2-methyl-5-phenyl-4-vinylfuran-3-carboxylate (4). Yellow liquid. R_f 0.31 (hexane/ethyl acetate=10:1). ^{1}H NMR ($CDCl_3$): δ 1.37 (t, *J*=7.1 Hz, 3H, CH_3), 2.59 (s, 3H, CH_3), 4.32 (q, *J*=7.1 Hz, 2H, CH_2), 5.35 (dd, *J*=11.5 Hz, *J*=1.7 Hz, 1H, *trans*-CH), 5.53 (dd, *J*=17.8 Hz, *J*=1.7 Hz, 1H, *cis*-CH), 6.85 (dd, *J*=17.8 Hz, *J*=11.5 Hz, 1H, CH), 7.27–7.40 (m, 3H, *m*,*p*-Ph), 7.68–7.71 (m, 2H, *o*-Ph). ^{13}C NMR ($CDCl_3$): δ 14.3 (CH_3, CH_3, two overlapping peaks), 60.2 (CH_2), 114.5 (3-C), 119.1 (CH_2), 126.8 (*o*-Ph), 127.7 (CH), 127.8 (*p*-Ph), 128.4 (*m*-Ph), 130.7 (4-C), 148.1 (5-C), 158.3 (2-C), 164.4 (CO). IR (neat): 2984 m, 1710 s, 1634 w, 1607 m, 1583 w, 1492 m, 1446 m, 1401 m, 1384 m, 1353 w, 1222 bs, 1094 bs, 1029 w, 985 w, 914 m, 844 w, 765 m, 723 w, 692 m, 660 w, 598 w, 505 w, 368 bw cm^{-1}. MS (70 eV): *m/z* (relative intensity, %) 257 (M^++1, 20), 256 (M^+, 100), 255 (11), 228 (13), 227 (65), 211 (26), 210 (25), 209 (25), 184 (10), 183 (61), 182 (20), 181 (22), 169 (11), 168 (54), 155 (55), 154 (15), 153 (26), 152 (12), 141 (23), 140 (16), 139 (17), 129 (10), 128 (15), 115 (26), 105 (75), 91 (11), 77 (92), 76 (10), 69 (20), 63 (12), 55 (12), 51 (37), 50 (13). Found: C 74.60; H 6.33. Anal. Calcd for $C_{16}H_{16}O_3$: C 74.98; H 6.29; O 18.73. HRMS Found: 256.1104. Calcd for $C_{16}H_{16}O_3$: 256.1100.

Ethyl 4-benzylidene-5-hydroxymethyl-2-methyl-4,5-dihydrofuran-3-carboxylate (5). This product was purified by column chromatography on silica gel (eluent; hexane/ethyl acetate=2:1) to give a yellow liquid (238 mg, 87% yield). R_f 0.16 (hexane/ethyl acetate=2:1). ^{1}H NMR ($CDCl_3$): δ 0.68 (t, *J*=7.0 Hz, 3H, CH_3), 1.95 (s, 1H, OH), 2.26 (s, 3H, CH_3), 3.63 (m, 2H, CH_2), 3.86 (d, *J*=5.0 Hz, 2H, CH_2), 5.29 (dt, *J*=5.0 Hz, *J*=2.7 Hz, 1H, 5-H), 6.07 (d, *J*=2.7 Hz, 1H, CH), 7.08–7.28 (m, 5H, Ph). ^{13}C NMR ($CDCl_3$): δ 13.2 (CH_3), 14.5 (CH_3), 60.2 (CH_2), 66.1 (CH_2), 88.2 (5-C), 108.4 (3-C), 114.1 (CH), 126.3, 127.7, 127.8 (Ph), 136.2 (*ipso*-Ph), 138.3 (4-C), 165.1 (CO), 174.4 (2-C). IR (neat): 3466 bm, 2986 bm, 1704 s, 1613 s, 1448 m, 1410 m, 1369 m, 1306 m, 1262 m, 1241 m, 1140 s, 1093 m, 963 m, 921 w, 833 w, 764 m, 696 m, 604 bw cm^{-1}. MS (70 eV): *m/z* (relative intensity, %) 275 (M^++1, 6), 274 (M^+, 28), 243 (37), 215 (11), 200 (12), 199 (100), 198 (67), 141 (27), 139 (10), 137 (29), 129 (14), 128 (29), 127 (14), 115 (39), 105 (16), 91 (15), 77 (20), 63 (16), 51 (16). HRMS Found: 274.1208. Calcd for $C_{16}H_{18}O_4$: 274.1205.

1-(2-Methyl-5-phenyl-4-vinylfuran-3-yl) ethanone (7). Yellow liquid. R_f 0.14 (hexane/ethyl acetate=10:1). ^{1}H NMR ($CDCl_3$): δ 2.43 (s, 3H, CH_3), 2.57 (s, 3H, CH_3), 5.40 (dd, *J*=17.6 Hz, *J*=2.0 Hz, 1H, CH), 5.45 (dd, *J*=10.9 Hz, *J*=2.0 Hz, 1H, CH), 6.84 (dd, *J*=17.6 Hz, *J*=10.9 Hz, 1H, CH), 7.26–7.40 (m, 3H, *m*,*p*-Ph), 7.67–7.70 (m, 2H, *o*-ph). ^{13}C NMR ($CDCl_3$): δ 14.4 (CH_3), 31.2 (CH_3), 119.2 (3-C), 120.4 (CH_2), 124.0 (*ipso*-ph), 126.5 (*o*-ph), 127.7 (*p*-ph), 128.4 (CH, *m*-ph, two overlapping peaks), 130.4 (4-C), 147.7 (5-C), 156.5 (2-C), 196.0 (CO). IR (neat): 3088 w, 3060 w, 3004 w, 2928 w, 2860 w, 1676 s, 1636 m, 1608 m, 1576 s, 1558 s, 1494 m, 1428 m, 1392 s, 1308 m, 1258 w, 1218 m, 1158 w, 1124 m, 1070 s, 1030 m, 994 m, 954 s, 916 m, 770 s, 742 m, 694 s,

664 m, 636 w, 568 w, 508 w cm^{-1}. MS (70 eV): *m/z* (relative intensity, %) 227 (M^++1, 15), 226 (M^+, 97), 225 (77), 211 (23), 183 (56), 165 (24), 155 (38), 153 (13), 152 (10), 141 (39), 139 (18), 115 (45), 105 (55), 91 (19), 77 (100), 76 (19), 63 (20), 55 (32), 52 (12), 51 (72), 50 (21). Found: C 79.49; H 6.43. Anal. Calcd for $C_{15}H_{14}O_2$: C 79.62; H 6.24; O 11.14. HRMS Found: 226.0992. Calcd for $C_{15}H_{14}O_2$: 226.0994.

3-Acetyl-4-benzylidene-5-hydroxymethyl-2-methyl-4,5-dihydrofuran (8). Yellow liquid. R_f 0.14 (hexane/ethyl acetate=2:1). ^{1}H NMR ($CDCl_3$): δ 1.54 (s, 3H, CH_3), 2.16 (s, 3H, CH_3), 2.27 (bs, 1H, OH), 3.86 (d, *J*=5.0 Hz, 2H, CH_2), 5.28 (dt, *J*=5.0 Hz, *J*=2.4 Hz, 1H, 5-H), 6.11 (d, *J*=2.4 Hz, 1H, CH), 7.12–7.31 (m, 5H, Ph). ^{13}C NMR ($CDCl_3$): δ 14.4 (CH_3), 29.8 (CH_3), 66.0 (CH_2), 87.9 (5-C), 114.1 (CH), 118.0 (3-C), 126.9 (*p*-ph), 127.8 (*m*-ph), 128.6 (*o*-ph), 138.1 (4-C, *ipso*-ph, two overlapping peaks), 172.0 (2-C), 197.6 (CO). IR (neat): 3428 bm, 3028 w, 2928 m, 2864 w, 1668 bs, 1590 bs, 1496 m, 1450 m, 1402 s, 1372 m, 1328 m, 1304 m, 1278 m, 1234 m, 1136 m, 1080 bm, 1026 bm, 946 m, 902 w, 840 w, 748 bw, 700 m, 650 w, 626 w, 602 w, 544 w, 506 bw cm^{-1}. MS (70 eV): *m/z* (relative intensity, %) 245 (M^++1, 14), 244 (M^+, 70), 226 (10), 214 (36), 213 (100), 201 (11), 199 (13), 143 (20), 128 (19), 91 (12), 43 (37). HRMS Found: 244.1106. Calcd for $C_{15}H_{16}O_3$: 244.1099.

Ethyl 4-isopropenyl-2-methyl-5-phenylfuran-3-carboxylate (10). White solid; mp 53–54°C. R_f 0.34 (hexane/ethyl acetate=10:1). ^{1}H NMR ($CDCl_3$): δ 1.34 (t, *J*=7.2 Hz, 3H, CH_3), 2.10 (s, 3H, CH_3), 2.62 (s, 3H, CH_3), 4.29 (q, *J*=7.2 Hz, 2H, CH_2), 5.00 (m, 1H, *trans*-CH), 5.26 (m, 1H, *cis*-CH), 7.21–7.37 (m, 3H, *m*,*p*-Ph), 7.73–7.76 (m, 2H, *o*-Ph). ^{13}C NMR ($CDCl_3$): δ 14.1 (CH_3), 14.3 (CH_3), 27.8 (CH_3), 60.0 (CH_2), 115.1 (3-C), 116.9 (CH_2), 123.9 (4-C), 125.1 (*o*-Ph), 127.2 (*p*-Ph), 128.4 (*m*-Ph), 130.6 (*ipso*-Ph), 138.3 (C), 145.9 (5-C), 158.1 (2-C), 164.0 (CO). IR (KBr): 2984 bm, 1710 s, 1650 w, 1608 w, 1564 w, 1496 m, 1424 bm, 1372 m, 1320 s, 1238 w, 1202 s, 1096 s, 1070 m, 1038 m, 1008 w, 974 w, 918 w, 898 m, 848 w, 788 w, 768 m, 726 w, 694 m, 666 w, 628 w, 574 w, 524 w cm^{-1}. MS (70 eV): *m/z* (relative intensity, %) 271 (M^++1, 6.3), 270 (M^+, 44), 255 (14), 241 (17), 227 (17), 225 (13), 223 (14), 209 (28), 197 (25), 196 (16), 195 (16), 183 (36), 182 (31), 181 (23), 165 (10), 155 (32), 154 (13), 153 (26), 152 (29), 141 (10), 139 (10), 128 (15), 115 (19), 105 (48), 91 (14), 77 (100), 65 (11), 63 (13), 51 (41), 50 (10). Found: C 75.36; H 6.83. Anal. Calcd for $C_{17}H_{18}O_3$: C 75.53; H 6.71; O 17.76. HRMS Found: 270.1254. Calcd for $C_{17}H_{18}O_3$: 270.1256.

Ethyl 4-benzylidene-5-hydroxymethyl-2,5-dimethyl-4,5-dihydrofuran-3-carboxylate (11). Yellow liquid. R_f 0.16 (hexane/ethyl acetate=2:1). ^{1}H NMR (acetone-d_6): δ 0.58 (t, *J*=7.0 Hz, 3H, CH_3), 1.41 (s, 3H, CH_3), 2.13 (s, 3H, CH_3), 3.54 (m, 4H, CH_2, CH_2), 4.09 (t, *J*=6.3 Hz, 1H, OH), 5.92 (s, 1H, CH), 7.00–7.21 (m, 5H, Ph). ^{13}C NMR (acetone-d_6): δ 13.6 (CH_3), 14.5 (CH_3), 23.1 (CH_3), 60.2 (CH_2), 69.2 (CH_2), 93.8 (5-C), 108.5 (3-C), 114.1 (CH), 126.4 (*p*-Ph), 128.2 (*o*-Ph), 128.7 (*m*-Ph), 140.2 (*ipso*-Ph), 142.7 (4-C), 165.7 (CO), 172.7 (2-C). IR (neat): 3450 bm, 2982 bm, 1705 bs, 1612 s, 1494 w, 1476 w, 1449 m, 1408 m, 1370 m, 1297 s, 1251 m, 1224 m, 1175 m, 1134 s, 1089 s, 1057 bs, 1023 m, 993 m, 917 w, 889 w, 857 w, 830 w, 768 w, 745 m, 697 m, 605 w, 586 w, 566 w, 543 w, 507 w, 476 w cm^{-1}. MS (70 eV): *m/z* (relative intensity, %) 289 (M^++1, 12), 288 (M^+, 57), 258 (35), 257 (100), 229 (17), 214 (13), 213 (75), 212 (49), 211 (13), 43 (20). HRMS Found: 288.1357. Calcd for $C_{17}H_{20}O_4$: 288.1362.

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