

# Effects of $\alpha$ -*tert*-Butyl Group Substitution on the Reactivity and Dimerization Products of Furan-Based *o*-Quinodimethanes<sup>1</sup>

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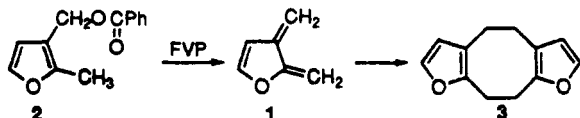
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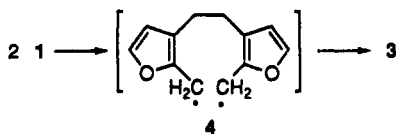
Flash vacuum pyrolysis (FVP) of 2-neopentyl-3-furylmethyl benzoate (8) produces 3-methylene-2-(*tert*-butylmethylene)-2,3-dihydrofuran (5), the major product as shown by low-temperature <sup>1</sup>H NMR spectroscopy. Upon warming to room temperature, 5 dimerizes giving mostly two stereoisomeric [4 + 2] dimers 11a and 11b in addition to a small amount of the [4 + 4] dimer 12. FVP of a mixture of the two [4 + 2] dimers 11a and 11b gives the thermodynamically more stable [4 + 4] dimer 12. The rate constants for the dimerization of 5 in solution at temperatures from -29 to +5 °C were determined by <sup>1</sup>H NMR spectroscopy. The rate constants and activation parameters ( $\Delta H^\ddagger = 10.8$  kcal/mol,  $\Delta S^\ddagger = -28.8$  eu) are very similar to those reported for the unsubstituted furan-based *o*-quinodimethane. FVP of (2-methyl-3-furyl)(*tert*-butyl)methyl benzoate (13) and (2-neopentyl-3-furyl)(*tert*-butyl)methyl benzoate (18) give as the major product, 2-methylene-3-(*tert*-butylmethylene)-2,3-dihydrofuran (6) and 2,3-bis(*tert*-butylmethylene)-2,3-dihydrofuran (7), respectively. Compounds 6 and 7, in contrast to 5, are stable at room temperature apparently because for each of these compounds a bulky *tert*-butyl group is on the more reactive methylene, the 3-methylene. These results offer further support for the mechanism for the dimerization of furan-based *o*-quinodimethanes which proceeds in two steps via a transient diradical intermediate.

## Introduction

During the past decade our research group has been actively studying 2,3-dimethylene-2,3-dihydrofuran (1), the furan-based *o*-quinodimethane (*o*-QDM).<sup>2-5</sup> Compound 1, conveniently prepared by the flash vacuum pyrolysis (FVP) of 2-methyl-3-furylmethyl benzoate (2), dimerizes rapidly in solution at temperatures above -30 °C to form 3, the head-to-head [4 + 4] dimer, in high yield.<sup>2</sup> On the basis of a secondary deuterium kinetic

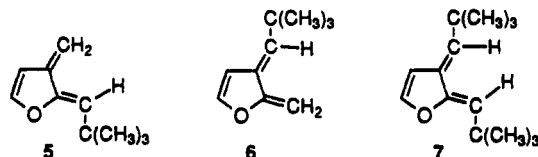


isotope effect study, it was concluded that the cyclization involves rate-determining formation of diradical 4, fol-



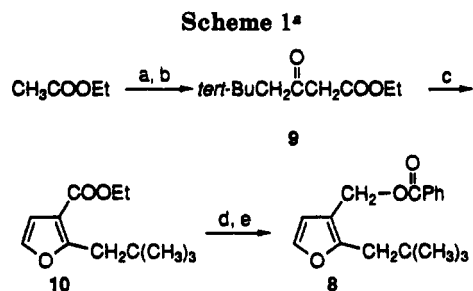
lowed by rapid closure of the diradical to give the dimer.<sup>3,5a</sup> In this mechanism, only the 3-methylene is directly involved in the rate-determining step to form 4, but the 2-methylene is involved in the product forming step. Thus we expected that a *tert*-butyl group on the 2-methylene

position would not affect the rate of dimerization but could affect the type of products formed, and we expected that a *tert*-butyl group on the 3-methylene position would retard the rate of dimerization. In this paper we report the results of a study of the dimerization of 5-7. The results are consistent with our expectations and offer additional support for the proposed two-step mechanism.



## Results

The synthesis of 2-neopentyl-3-furylmethyl benzoate (8) is outlined in Scheme 1. Ethyl *tert*-butylacetoacetate



<sup>a</sup> (a) LiN(Pr-*i*)(C<sub>8</sub>H<sub>11</sub>-cyclo); (b) *tert*-BuCH<sub>2</sub>COCl; (c) ClCH<sub>2</sub>CHO, pyridine; (d) LiAlH<sub>4</sub>; (e) PhCOCl, Et<sub>3</sub>N.

(9) was prepared by treating ethyl acetate with a base followed by treatment with *tert*-butylacetyl chloride.<sup>6</sup> Cyclization of ester 9 and chloroacetaldehyde gave 10<sup>7</sup> which was reduced by lithium aluminum hydride and the resulting alcohol was converted to 8 by treatment with

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(1) (a) Presented in part at the 196th National Meeting of the American Chemical Society, Los Angeles, California, September 1988, paper ORGN 190. (b) Based on work by Y. J. H. in partial fulfillment of the requirements for the Ph.D. degree at Iowa State University.

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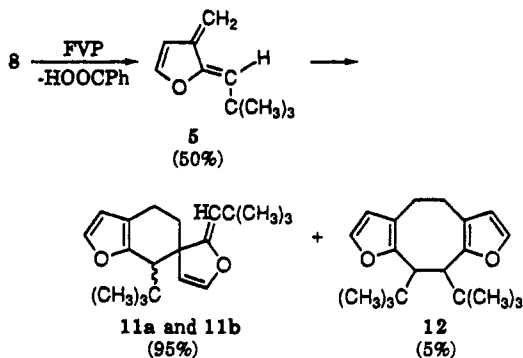
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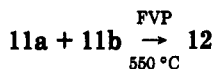
(6) Rathke, M. W.; Deitch, J. *Tetrahedron Lett.* 1971, 2953.

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benzoyl chloride. Compound **5** was prepared by the FVP of **8** using the method previously reported for the preparation of **1**<sup>2,3</sup> at temperatures from 520–650 °C and pressures of *ca.* 10<sup>-5</sup> torr. A <sup>1</sup>H NMR spectrum of the pyrolysis product dissolved in CDCl<sub>3</sub>/CS<sub>2</sub> at -60 °C revealed only one isomer, presumably the less crowded *Z* isomer. The yield of **5** was 50% as determined by <sup>1</sup>H NMR analysis using an internal standard. Upon warming to room temperature, **5** dimerized giving approximately equal amounts of two stereoisomeric [4 + 2] dimers **11a** and **11b** in addition to a small amount of the [4 + 4] dimer **12**. The constitution of the [4 + 2] dimers was determined by 2-D <sup>1</sup>H NMR spectroscopy<sup>9</sup> and is similar to that of the [4 + 2] dimer obtained from 2,3-dimethylene-2,3-dihydrobenzofuran.<sup>4</sup> Dimer **12** appears to be a single stere-



oisomer, presumably the *trans* isomer. The combined yield of the three dimers from **8** was 40%. FVP of a mixture of the two [4 + 2] dimers **11a** and **11b** gave the more thermodynamically stable [4 + 4] dimer **12**.



The rate constants for the dimerization of **5**, presented in Table 1, were determined by measuring the rate of

**Table 1. Rate Constants for the Dimerization of 2-(*tert*-Butylmethylene)-3-methylene-2,3-dihydrofuran (**5**)**

temperature, °C	$k_2$ ( $\times 10^3$ ), L mol <sup>-1</sup> s <sup>-1</sup>
5.0	9.82 ± 0.14
-6.0	4.18 ± 0.04
-12.0	2.74 ± 0.01
-22.0	1.11 ± 0.01
-29.0	0.57 ± 0.01

disappearance of **5** (in 1:1 CDCl<sub>3</sub>/CS<sub>2</sub> with BrCH<sub>2</sub>CH<sub>2</sub>Br as an internal standard) by low-temperature <sup>1</sup>H NMR spectroscopy, using the method previously reported.<sup>3</sup> In Table 2 are presented the activation parameters derived

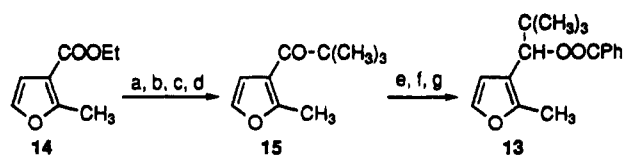
**Table 2. Activation Parameters for the Dimerization of 2-(*tert*-Butylmethylene)-3-methylene-2,3-dihydrofuran (**5**)**

$E_a$ , kcal/mol	log $A$ ( $A$ , L mol <sup>-1</sup> s <sup>-1</sup> )	$\Delta H^\ddagger$ , kcal/mol	$\Delta S^\ddagger$ , eu
11.3 ± 0.2	6.86 ± 0.13	10.8 ± 0.2	-28.8 ± 0.6

from these data.

The synthesis of (2-methyl-3-furyl)(*tert*-butyl)methyl benzoate (**13**) is outlined in Scheme 2. Ester **14**<sup>7</sup> was converted to the acid chloride which was then converted to ketone **15** by treatment with *tert*-butylmagnesium

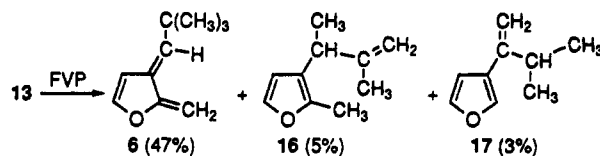
**Scheme 2<sup>a</sup>**



<sup>a</sup> (a) NaOH; (b) HCl; (c) SOCl<sub>2</sub>; (d) *tert*-BuMgCl, CuI; (e) LiAlH<sub>4</sub>; (f) *n*-BuLi; (g) PhCOCl.

chloride and copper(I) iodide.<sup>9,10</sup> Ketone **15** was reduced to the alcohol which was converted to **13** by treatment with *n*-butyllithium and then benzoyl chloride.

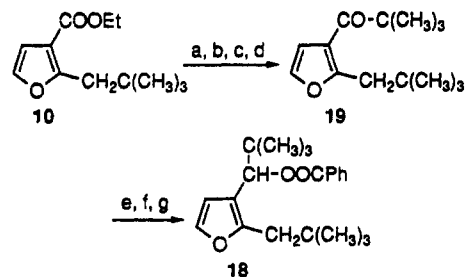
Compound **6** was prepared by the FVP of **13** at temperatures from 460–510 °C. The <sup>1</sup>H NMR spectrum of the pyrolysis product showed one *o*-quinodimethane (47%), presumably the less crowded *E* isomer **6**, along with two minor isomers, **16** (5%) and **17** (3%). Compound



**6** is so unreactive that it can be stored in solution for weeks in the refrigerator. Attempts to dimerize **6** in solution at temperatures from 20–35 °C resulted in slow decomposition of **6** but no dimers were detected.

The synthesis of (2-neopentyl-3-furyl)(*tert*-butyl)methyl benzoate (**18**) is outlined in Scheme 3. Ester **10** was

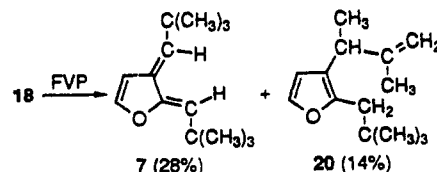
**Scheme 3<sup>a</sup>**



<sup>a</sup> (a) NaOH; (b) HCl; (c) SOCl<sub>2</sub>; (d) *tert*-BuMgCl, CuI; (e) LiAlH<sub>4</sub>; (f) *n*-BuLi; (g) PhCOCl.

converted to ketone **19** by the reaction sequence used to prepare ketone **15** from ester **14**. Ketone **19** was converted to ester **18** by the same procedure used to prepare ester **13** from ketone **15**.

The FVP of **18** was carried out at 530 °C. GC-MS and <sup>1</sup>H NMR analysis of the pyrolysate showed that the major product in 28% yield was a single *o*-quinodimethane, presumably the less crowded *2Z,3E* isomer **7**. In addition to **7**, isomer **20** was also produced in 14% yield. Compound **7** was even less reactive than **6**.



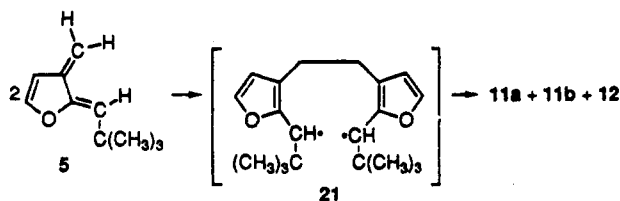
## Discussion

Both the dimerization products and the dimerization rate constants of **5** are consistent with the two-step

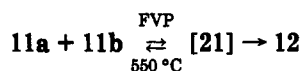
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mechanism proposed for the dimerization of 2,3-dimethylene-2,3-dihydrofuran (1). The expected diradical from 5 is 21 which readily accounts for the formation of [4 +



2] dimers 11a and 11b and [4 + 4] dimer 12. Presumably the bulky *tert*-butyl groups retard the rate of formation of the [4 + 4] dimer 12 and allow formation of the [4 + 2] dimers 11a and 11b to become competitive. The conversion of the [4 + 2] dimers 11a and 11b to the [4 + 4] dimer 12 by FVP offers further support for the constitution assigned to 11a and 11b. Evidently under these conditions the [4 + 2] dimers form diradical 21 which produces in highest yield the most thermodynamically stable dimer, [4 + 4] dimer 12.



The rate of formation of diradical 21 from *o*-quinodimethane 5 should be similar to the rate of formation of diradical 4 from the unsubstituted *o*-quinodimethane 1 since the bulky *tert*-butyl groups are on the 2-methylene groups which are not directly attached to the bond-formation site in the rate-determining step. The observed rate constants (e.g.,  $k = 5.7 \times 10^{-4} \text{ L mol}^{-1} \text{ s}^{-1}$  at  $-29^\circ\text{C}$ ) and activation parameters ( $\Delta H^\ddagger = 10.8 \text{ kcal/mol}$ ;  $\Delta S^\ddagger = -28.8 \text{ eu}$ ) are very similar to those reported for the parent system, 1 ( $k = 6.2 \times 10^{-4} \text{ L mol}^{-1} \text{ s}^{-1}$  at  $-30^\circ\text{C}$ ;  $\Delta H^\ddagger = 10.2 \text{ kcal/mol}$ ;  $\Delta S^\ddagger = -30.9 \text{ eu}$ ).<sup>3</sup> Clearly the *tert*-butyl group of 5 has no significant effect on the rate of dimerization of 5. This observation implies that having a *tert*-butyl group on the 2-methylene group does not alter the mechanism. The first step, the diradical formation step that involves only the 3-methylene position, is still the rate-determining step. Increasing the steric hindrance at the 2-methylene position changes only the product distribution from [4 + 4] to [4 + 2] dimers, not the overall reaction rate.

The reactivity of both 6 and 7 are also consistent with the proposed two-step mechanism for the dimerization of furan-based *o*-quinodimethanes. Both 6 and 7 have a bulky *tert*-butyl group on the more reactive methylene, the 3-methylene, which should significantly retard their rate of dimerization, and indeed both *o*-quinodimethanes are stable at room temperature.

In addition to the expected *o*-quinodimethanes, the FVP of 13 and 18 gave rise to low yields of isomers. At this time it is not clear how these products are formed. The mechanism of these transformations are under investigation.

## Experimental Section

**Methods and Materials.** The pyrolysis apparatus has been previously described.<sup>11</sup> <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on JOEL FX-90Q or Nicolet-300 spectrometers. Chemical shifts are recorded in parts per million ( $\delta$ ) from tetramethylsilane (TMS). High resolution mass spectra were measured with an Associated Electronics Industries MS-902 instrument. Gas

chromatography/mass spectroscopy (GC/MS) was performed with a Finnigan 4000 instrument and an INCOS data system. GLC analyses were performed with a Hewlett-Packard HP 5840A instrument. The dimerization kinetic experiments were performed on a Varian VXR-300 <sup>1</sup>H NMR spectrometer equipped with a FTS System air chiller at temperatures ranging from  $-30$  to  $10^\circ\text{C}$ . Temperatures were calibrated using a methanol standard supplied by Varian.

**2-Neopentyl-3-furylmethyl Benzoate (8).** Using the procedure of Rathke and Deitch,<sup>6</sup> a quantity of 3.1 g (35 mmol) of ethyl acetate and 4.7 g (35 mmol) of *tert*-butylacetyl chloride was converted to 5.5 g (30 mmol, 85.7% recovered after removal of the extraction solvent; the material was used without further purification) of ethyl *tert*-butylacetoacetate (9): <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  4.15 (q,  $J = 7.5 \text{ Hz}$ , 2 H), 3.38 (s, 2 H), 2.40 (s, 2 H), 1.25 (t,  $J = 7.5 \text{ Hz}$ , 3 H), 1.10 (s, 9 H).

Using the procedure previously described for the synthesis of ethyl 2-methyl-3-furoate<sup>2,7</sup> (14), a quantity of 5.4 g (29 mmol) of 9 was converted to 3.3 g (15.7 mmol, 54%) of ethyl 2-neopentyl-3-furoate (10): bp  $45-7^\circ\text{C}$  (0.3 mm); IR (thin film) 1720, 1360, 1305, 1275, 1150  $\text{cm}^{-1}$ ; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  7.20 (d,  $J = 2 \text{ Hz}$ , 1 H), 6.61 (d,  $J = 2 \text{ Hz}$ , 1 H), 4.20 (q,  $J = 8.0 \text{ Hz}$ , 2 H), 2.82 (s, 2 H), 1.38 (t,  $J = 8.0 \text{ Hz}$ , 3 H), 1.02 (s, 9 H).

A solution of 3.0 g (14.3 mmol) of 10 in 10 mL of ether was reduced with LiAlH<sub>4</sub>, using the procedure described<sup>2</sup> previously for the synthesis of 2-methyl-3-furylmethyl alcohol, to give 2.3 g (13.7 mmol, 96%) of 2-neopentyl-3-furylmethyl alcohol: <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  7.35 (d,  $J = 2 \text{ Hz}$ , 1 H), 6.40 (d,  $J = 2 \text{ Hz}$ , 1 H), 4.48 (s, 2 H), 2.52 (s, 2 H), 1.68 (br, 1 H), 0.95 (s, 9 H). A solution of 2.3 g (13.7 mmol) of this alcohol and 2.1 g (20.5 mmol) of triethylamine in 40 mL of ether was esterified with benzoyl chloride, using the procedure previously described<sup>2</sup> for the synthesis of 2-methyl-3-furylmethyl benzoate (2), to yield 3.3 g (12.1 mmol, 88%) of 8: IR (thin film) 1720, 1460, 1365, 1268, 1105  $\text{cm}^{-1}$ ; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  8.15-7.88 (m, 2 H), 7.56-7.32 (m, 3 H), 7.28 (d,  $J = 2 \text{ Hz}$ , 1 H), 6.38 (d,  $J = 2 \text{ Hz}$ , 1 H), 5.18 (s, 2 H), 2.58 (s, 2 H), 0.99 (s, 9 H); high-resolution mass spectrum, calcd for C<sub>17</sub>H<sub>20</sub>O<sub>3</sub> 272.14125, measured 272.14131.

**(2-Methyl-3-furyl)(*tert*-butyl)methyl Benzoate (13).** A mixture of 50 g (0.36 mol) of ethyl 2-methyl-3-furoate<sup>7</sup> (14) in 200 mL of 20% sodium hydroxide was heated to reflux for 2 h. After the mixture was allowed to cool to room temperature, it was acidified with 100 mL of concentrated HCl with rapid stirring. A white solid formed which was collected by suction filtration. The solid was dried under vacuum to give 43 g (0.34 mol, 95%) of 2-methyl-3-furoic acid: mp  $95-97^\circ\text{C}$ ; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  11.52 (br, 1 H), 2.30 (d,  $J = 2 \text{ Hz}$ , 1 H), 6.71 (d,  $J = 2 \text{ Hz}$ , 1 H), 2.62 (s, 3 H). A 10.6 g (84 mmol) quantity of this acid was added to 49.0 g (410 mmol) of thionyl chloride and the mixture was stirred at  $40^\circ\text{C}$  for 24 h. The excess thionyl chloride was removed by simple distillation and the remaining dark oil was distilled under reduced pressure ( $65-67^\circ\text{C}/20 \text{ mm}$  of Hg) to yield 10.6 g (73 mmol, 87.3%) of 2-methyl-3-furoyl chloride: IR (thin film) 1760, 1560, 1525, 1270, 1210  $\text{cm}^{-1}$ ; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  7.29 (d,  $J = 2 \text{ Hz}$ , 1 H), 6.70 (d,  $J = 2 \text{ Hz}$ , 1 H), 2.51 (s, 3 H). A quantity of 34.5 mL of *tert*-butylmagnesium chloride (69 mmol, 2 M in ether) was added dropwise to a suspension of 9.0 g (62 mmol) of 2-methyl-3-furyl chloride and 17.7 g (93 mmol) of copper iodide in 80 mL of ether at  $-78^\circ\text{C}$ .<sup>9,10</sup> The mixture was stirred and allowed to reach room temperature overnight. The resulting green suspension was poured into 50 mL of ice-cooled 2 N HCl. The layers were separated and the organic layer was washed with 2 N HCl, NaHCO<sub>3</sub>, and brine. After the organic layer was dried and concentrated, 8.5 g (51 mmol, 82.5%) of 2-methyl-3-furyl *tert*-butyl ketone (15) was recovered: <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  7.20 (d,  $J = 2 \text{ Hz}$ , 1 H), 6.78 (d,  $J = 2 \text{ Hz}$ , 1 H), 2.52 (s, 3 H), 1.27 (s, 9 H).

An 8.5 g (51 mmol) quantity of ketone 15 was reduced with LiAlH<sub>4</sub> using the procedure described previously<sup>2</sup> to give 7.7 g (46 mmol, 90.2%) of (2-methyl-3-furyl)(*tert*-butyl)methyl alcohol: IR (thin film) 3400 (br), 1625, 1510, 1425, 1150, 985

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cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.32 (d, *J* = 2 Hz, 1 H), 6.43 (d, *J* = 2 Hz, 1 H), 4.35 (br, 1 H), 2.28 (s, 3 H), 1.85 (br, 1 H), 0.95 (s, 9 H). To a solution of 4.0 g (24 mmol) of the alcohol in 80 mL of dry THF (LiAlH<sub>4</sub>), 12.5 mL of *n*-BuLi (2 M in hexane) was added via a syringe at 0 °C. The mixture was stirred for 10 min and 3.7 g (26 mmol) of benzoyl chloride was added dropwise. The resulting red mixture was allowed to sit overnight at room temperature. After the addition of 50 mL of water, the aqueous layer was extracted with ether (50 mL × 2) and the combined organic layer was washed with water, NaHCO<sub>3</sub>, and brine. Drying (MgSO<sub>4</sub>) and removal of the solvent followed by purification with column chromatography on silica gel (5% ether in hexane) gave 4.1 g (15 mmol, 62.5%) of 13: IR (thin film) 1710, 1309, 1260, 1095, 1112 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 8.12–7.90 (m, 2 H), 7.57–7.35 (m, 3 H), 7.21 (d, *J* = 2 Hz, 1 H), 6.32 (d, *J* = 2 Hz, 1 H), 5.76 (s, 1 H), 2.37 (s, 3 H), 1.08 (s, 9 H); high-resolution mass spectrum, calcd for C<sub>17</sub>H<sub>20</sub>O<sub>3</sub> 272.14125, measured 272.14089.

**(2-Neopentyl-3-furyl)(*tert*-butyl)methyl Benzoate (18).** A quantity of 1.8 g (8.6 mmol) of ethyl 2-neopentyl-3-furoate (10) was converted to 0.8 g (3.6 mmol, 41.9%) of 2-neopentyl-3-furyl *tert*-butyl ketone (19) using the multistep synthesis described above for the synthesis of ketone 15. For 19: <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.42 (d, *J* = 2 Hz, 1 H), 6.48 (d, *J* = 2 Hz, 1 H), 3.08 (s, 2 H), 1.48 (s, 9 H), 1.12 (s, 9 H).

A 0.8 g (3.6 mmol) quantity of ketone 19 was reduced with LiAlH<sub>4</sub>, using the procedure described previously<sup>2</sup> to give 0.65 g (2.9 mmol, 80.6%) of (2-neopentyl-3-furyl)(*tert*-butyl)methyl alcohol: <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.29 (d, *J* = 2 Hz, 1 H), 6.38 (d, *J* = 2 Hz, 1 H), 4.31 (s, 1 H), 2.48 (s, 2 H), 1.52 (br, 1 H), 1.00 (s, 9 H), 0.96 (s, 9 H). A 0.62 g (2.8 mmol) quantity of this alcohol was esterified with *n*-BuLi and benzoyl chloride using the procedure described above for the synthesis of 13 to give 0.7 g (2.1 mmol, 75.0%) of 18: IR (thin film); <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 8.35–8.10 (m, 2 H), 7.64–7.46 (m, 3 H), 7.32 (d, *J* = 2 Hz, 1 H), 6.47 (d, *J* = 2 Hz, 1 H), 5.80 (s, 1 H), 2.72 (AB pattern, *J* = 15 Hz, 2 H), 1.10 (s, 9 H), 1.02 (s, 9 H); high-resolution mass spectrum, calcd for C<sub>21</sub>H<sub>28</sub>O<sub>3</sub> 328.20385, measured 328.20353.

**General Pyrolysis Procedure.**<sup>11</sup> The pyrolyses were run at furnace temperatures from 400 to 800 °C. The sample chamber was heated to 60–70 °C and the system was evacuated to ca. 10<sup>-5</sup> Torr during the pyrolysis. A condenser cooled to ca. -20 °C was inserted between the quartz pyrolysis tube and the liquid nitrogen-cooled trap to collect the unreacted starting material and the benzoic acid formed as a byproduct. The liquid nitrogen-cooled trap was used to collect the products. Upon completion of the pyrolysis, the trap was warmed to -78 °C and carbon disulfide or deuteriochloroform was distilled into the trap through the side arm. Also added was a known amount of 1,2-dibromoethane as an internal standard for quantitative studies.

**Pyrolysis of 2-Neopentyl-3-furylmethyl Benzoate (8).** Pyrolyses were performed with ca. 0.2 g of 8 at 520, 580, and 650 °C using the general procedure. The pyrolysate was collected in 3 mL of 1:1 CS<sub>2</sub>/CDCl<sub>3</sub> from the trap and <sup>1</sup>H NMR spectrum of the product 3-methylene-2-*tert*-butylmethylene-2,3-dihydrofuran (5) was recorded at -60 °C: <sup>1</sup>H NMR (CDCl<sub>3</sub>/CS<sub>2</sub> 1:1, -60 °C) δ 6.77 (br, 1 H), 5.75 (d, *J* = 3 Hz, 1 H), 5.25 (s, 1 H), 4.96 (d, *J* = 1 Hz, 1 H), 4.74 (d, *J* = 1 Hz, 1 H), 1.15 (s, 9 H). Upon warming, 5 slowly dimerized to give mostly two stereoisomeric [4 + 2] dimers 11a and 11b (ca. 1:1) in addition to a small amount (5%) of [4 + 4] dimer 12. The mixture of 11a and 11b was purified by column chromatography (silica gel, hexane). The <sup>1</sup>H NMR signals of each dimer were partially separated by a COSY 2-D <sup>1</sup>H NMR analysis. For 11a: <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.22 (br, 1 H), 6.39 (d, *J* = 3 Hz, 1 H), 6.10 (br, 1 H), 5.25 (d, *J* = 3 Hz, 1 H), 4.21 (s, 1 H), 2.85–2.65 (m, 1 H), 2.75 (s, 1 H), 2.25–2.12 (m, 1 H), 1.83–1.52 (m, 2 H), 1.06 (s, 9 H), 0.97 (s, 9 H); GC/MS (70 eV) *m/e* (% base peak) 300.02 (16.25), 243.96 (10.26), 242.94 (43.00), 200 (11.42), 186.94 (25.04), 172.90 (25.67), 150.96 (11.05), 149.96 (67.45), 148.98 (31.70), 134.92 (61.47), 90.88 (39.33), 56.98 (100.00). For 11b: <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.22 (br, 1 H), 6.47 (d, *J* = 3 Hz, 1 H), 6.10 (br, 1 H), 5.02 (d, *J* = 3 Hz, 1 H), 4.27 (s, 1 H), 2.63 (s, 1 H), 2.45–2.38 (m, 1 H), 2.25–2.12 (m, 1 H), 1.83–1.52 (m, 2 H), 1.05 (s, 9 H), 1.03 (s, 9 H); GC/MS (70 eV) *m/e* (% base peak) 300.02 (23.79), 256.98 (11.16), 243.98 (11.18), 242.94 (48.66), 200.96 (13.75), 186.94 (19.34), 172.92 (12.79), 150.98 (16.03), 149.98 (94.10), 148.98 (45.97), 135.98 (10.62), 134.92 (100.00), 120.96

(19.01), 90.88 (41.14), 56.96 (80.59). Quantitative <sup>1</sup>H NMR analysis using dibromoethane as a standard indicated that the pyrolysis of 8 gave 5 in 50% yield and the conversion of 5 to dimers 11a, 11b, and 12 was about 90%.

**Pyrolysis of Dimers 11a and 11b.** A quantity of 50 mg (0.17 mmol) of the mixture of dimers 11a and 11b was pyrolyzed at 550 °C in the normal manner except without the condenser. GC and <sup>1</sup>H NMR analyses of the pyrolysate showed that [4 + 4] dimer 12 was the major product. The crude product was purified by column chromatography (silica gel, hexane) to give 32 mg (0.11 mmol, 62.7%) of 12: <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.20 (d, *J* = 1.5 Hz, 1 H), 6.15 (d, *J* = 1.5 Hz, 1 H), 3.14 (s, 2 H), 2.86 (m, 2 H), 2.54 (m, 2 H), 0.87 (s, 18 H); GC/MS (70 eV) *m/e* (% base peak) 300.02 (3.13), 242.94 (12.76), 187.94 (7.03), 186.92 (31.79), 172.88 (12.56), 114.90 (3.36), 57.06 (100.00); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 153.03, 137.95, 120.22, 115.78, 50.89, 37.60, 29.61, 27.34.

**Pyrolysis of (2-Methyl-3-furyl)(*tert*-butyl)methyl Benzoate (13).** A quantity of 300 mg (1.1 mmol) of 13 was pyrolyzed at 510 °C under the normal conditions. GC and <sup>1</sup>H NMR analyses of the crude pyrolysate at room temperature indicated that the monomer 2-methylene-3-(*tert*-butylmethylene)-2,3-dihydrofuran (6) was the major product (85%) along with ca. 15% of two monomeric byproducts 16 and 17. Compound 6: <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 6.77 (m, 1 H), 6.06 (d, *J* = 2.7 Hz, 1 H), 5.81 (s, 1 H), 4.68 (d, *J* = 2 Hz, 1 H), 4.52 (d, *J* = 2 Hz, 1 H), 1.16 (s, 9 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 160.89, 147.92, 130.44, 129.54, 104.86, 81.34, 33.68, 30.73; UV (CHCl<sub>3</sub>) γ<sub>max</sub> 318 nm, ε<sub>max</sub> = 2500. A mixture of 16 and 17 was purified by column chromatography (silica gel, hexane). Assignment of their structures was based on the analysis of the <sup>1</sup>H NMR spectrum of this mixture. Compound 16: <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.23 (d, *J* = 1.8 Hz, 1 H), 6.20 (d, *J* = 1.8 Hz, 1 H), 4.80 (d, *J* = 0.9 Hz, 1 H), 4.76 (d, *J* = 0.9 Hz, 1 H), 3.25 (q, *J* = 7.2 Hz, 1 H), 2.24 (s, 3 H), 1.66 (s, 3 H), 1.31 (d, *J* = 7.2 Hz, 3 H); GC/MS (70 eV) *m/e* (% base peak) 140.06 (100.00), 135.06 (58.03), 121.06 (19.00), 109.08 (54.36), 107.12 (24.45), 105.10 (13.49), 91.04 (34.90), 81.04 (13.52), 79.04 (28.48), 53.04 (14.54). Compound 17: <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.25 (d, *J* = 1.8 Hz, 1 H), 6.30 (d, *J* = 1.8 Hz, 1 H), 5.07 (d, *J* = 1.5 Hz, 1 H), 4.90 (d, *J* = 1.5 Hz, 1 H), 2.57 (m, *J* = 6.6 Hz, 1 H), 2.34 (s, 3 H), 1.08 (d, *J* = 6.6 Hz, 6 H); GC/MS (70 eV) *m/e* (% base peak) 150.08 (100.00), 135.06 (32.67), 121.06 (24.44), 107.12 (30.37), 105.10 (20.74), 91.04 (35.15), 79.06 (24.41), 53.04 (12.69). Quantitative <sup>1</sup>H NMR analysis using dibromomethane as a standard indicated that the pyrolysis of 13 gave 6 in 43% yield.

**Pyrolysis of (2-Neopentyl-3-furyl)(*tert*-butyl)methyl Benzoate (18).** A quantity of 200 mg (0.61 mmol) of 18 was pyrolyzed at 530 °C in the normal fashion. GC/MS and <sup>1</sup>H NMR of the pyrolysate indicated that 2,3-bis(*tert*-butylmethylene)-2,3-dihydrofuran (7) was the major product along with a rearranged isomeric compound 20 in a 2 to 1 ratio. The combined yield using dibromomethane as an internal standard was calculated to be 41%. The two compounds were not separated. Their <sup>1</sup>H NMR signals were distinguished and assigned individually. For 7: <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 6.75 (m, 1 H), 6.08 (d, *J* = 2.6 Hz, 1 H), 5.61 (s, 1 H), 5.12 (s, 1 H), 1.17 (s, 9 H), 1.15 (s, 9 H); GC/MS (70 eV) *m/e* (% base peak) 206.00 (36.37), 191.00 (19.56), 163.00 (11.24), 150.00 (24.16), 149.00 (100.00), 135.00 (19.56), 126.00 (25.13), 121.00 (21.15), 107.00 (13.36), 91.00 (18.67), 69.00 (11.50), 57.00 (29.03). For 20: <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.22 (m, 1 H), 6.17 (d, *J* = 2 Hz, 1 H), 4.80 (s, 1 H), 4.77 (s, 1 H), 3.22 (q, *J* = 7.1 Hz, 1 H), 2.45 (s, 2 H), 1.62 (s, 3 H), 1.35 (d, *J* = 7.1 Hz, 3 H), 1.03 (s, 9 H); GC/MS (70 eV) *m/e* (rel inten) 206.10 (46.24), 191.10 (12.51), 150.08 (62.73), 149.08 (100.00), 135.06 (41.23), 131.08 (17.12), 121.06 (24.61), 107.06 (22.70), 105.08 (16.73), 93.08 (15.08), 91.06 (24.71), 79.06 (16.78), 77.04 (14.46), 57.08 (72.55).

**Procedure for Measuring the Rate Constants of the Dimerization of 2-(*tert*-Butylmethylene)-3-methylene-2,3-dihydrofuran (5).** A quantity of 350 mg of 5 was pyrolyzed. To the pyrolysate (mainly 5) was added a solution (3 mL) of BrCH<sub>2</sub>-CH<sub>2</sub>Br (0.02294 M at 25 °C) in CDCl<sub>3</sub>/CS<sub>2</sub> (1:1) at liquid nitrogen temperature. The mixture was warmed to dry ice/acetone temperature and transferred to 5-mm <sup>1</sup>H NMR tubes under nitrogen. The <sup>1</sup>H NMR samples were then stored in a freezer at -90 °C until the kinetic experiments were performed. An NMR tube containing the pyrolysis products was inserted in the NMR sample probe which was kept at -50 °C. The magnet was

shimmed at  $-50\text{ }^{\circ}\text{C}$  and then the probe temperature was raised to the desired temperature. In order to equilibrate the sample temperature with that inside the probe, the NMR sample was allowed to stand for an extra 15 min before data collection started. The sample was kept inside the probe at the temperature for 3 h during which time, spectra were collected every 10 to 15 min. Concentration of the reactive **5** from each spectrum was calculated based on the calibrated concentration<sup>12</sup> of an added dibromoethane standard at the experimental temperature and from an

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(12) The actual volume of the solvent at low temperature was calibrated using the thermal expansion coefficient ( $\alpha = 0.00126/^{\circ}\text{C}$ ) which was determined by the equation  $\alpha = [(d_1/d_2) - 1]/\Delta t$ , where  $d_1$  is the density of the solvent at temperature  $t_1$ ,  $d_2$  is the density of the solvent at temperature  $t_2$ , and  $\Delta t = t_2 - t_1$ .<sup>13</sup>

(13) Marsden, C. *Solvent guide*; Wiley Interscience: New York, 1963, p 28.

average of three integrations. The rate constant of the dimerization reaction was then calculated from the rate of disappearance of the reactive monomer.

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**Supplementary Material Available:** Spectra ( $^1\text{H}$  and  $^{13}\text{C}$  NMR and IR) of new compounds described in this paper (15 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.