J. Am. Chem. Soc. 1981, 103, 6691-6695 6691

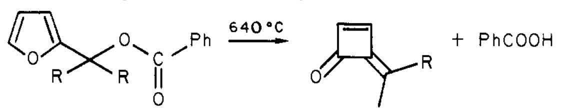
Preparation of 2,3-Dimethylene-2,3-dihydrofurans by the Flash Vacuum Pyrolysis of Substituted Furylmethyl Esters

Walter S. Trahanovsky,* Timothy J. Cassady,[1a] and Treacy L. Woods[1b]

Contribution from Ames Laboratory and Department of Chemistry, Iowa State University, Ames, Iowa 50011. *Received February 2, 1981*

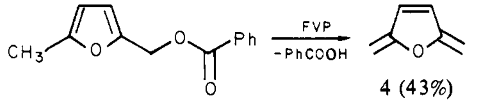
Abstract: Pyrolysis of 3-methylfurfuryl benzoate gives a 21% yield of 3-methyl-4-methylenecyclobutenone and a 24% yield of 4*H*,5*H*,9*H*,10*H*-cycloocta[1,2-*b*:6,5-*b*′]difuran (**8**), the head-to-head, [4 + 4] dimer of 2,3-dimethylene-2,3-dihydrofuran (**6**). A similar pyrolysis of 2-methyl-3-furylmethyl benzoate (**10**) gives **8** in 51% yield. Low-temperature ^{1}H and ^{13}C NMR spectral studies show that **6** is the intermediate in the formation of **8**. Compound **6** reacts with methyl acrylate to form a mixture of the isomeric Diels–Alder adducts. Pyrolysis of 2-methyl-3-furylmethyl-α,α-d_2 benzoate (**10**-d_2) gives **8**-d_4 via the intermediacy of **6**-d_2. Pyrolysis of 2,4-dimethyl-3-furylmethyl benzoate gives a 43% yield of 3,6-dimethyl-4*H*,5*H*,9*H*,10*H*-cycloocta[1,2-*b*:6,5-*b*′]difuran (**13**), the head-to-head, [4 + 4] dimer of 4-methyl-2,3-dimethylene-2,3-dihydrofuran (**14**). Low-temperature ^{1}H and ^{13}C NMR studies show that **14** is the intermediate in the formation of **13**. Compound **14** can be trapped with methyl acrylate to form a 3.1 to 1 ratio of the Diels–Alder adducts **15** and **16**. The structure proof of **15** and **16** involves the conversion of **15** to the commercially available, natural product menthofuran and **16** to isomenthofuran, which is synthesized by an independent route.

Several years ago we reported that the flash vacuum pyrolysis (FVP) of furfuryl benzoate (**1a**) gives a moderate yield (40%) of methylenecyclobutenone (**2a**) along with benzoic acid and some minor products.[2] In order to determine the scope of the reaction and to achieve a better understanding of its mechanism, the pyrolysis of a series of substituted furfuryl esters was undertaken.[3] A mechanism for the conversion of **1a** to **2a** was proposed on the basis of a deuterium-labeling experiment, **1b** to **2b**, and on a study of the products formed from the pyrolysis of 5-methylfurfuryl benzoate (**3**).[2b]



1a, R = H
b, R = D

2 (40%)



3

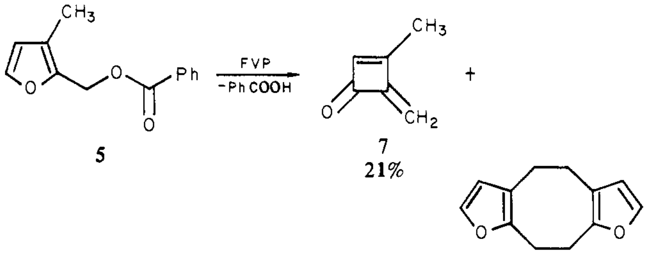
4 (43%)

As part of this study, the pyrolysis of 3-methylfurfuryl benzoate (**5**) was investigated because it was anticipated that pyrolysis of **5** would give 2,3-dimethylene-2,3-dihydrofuran (**6**). Compound **6** is a furan analogue of the *o*-quinodimethanes, an extensively investigated group of reactive intermediates.[4]

Results

The FVP of **5** at 620–640 °C and ca. 10^{-4} Torr produced a white product band in the cold trap at 77 K. Carbon disulfide was added to the trap and the product mixture was then slowly warmed to room temperature. The major products formed were 3-methyl-4-methylenecyclobutenone (**7**) and **8**, the head-to-head, [4 + 4] dimer of 2,3-dimethylene-2,3-dihydrofuran (**6**). These products were accompanied by the formation of benzoic acid and a substantial amount of a white polymer.

The structure of **7** was indicated by its spectral properties. The ^{1}H NMR spectrum included a doublet for the methyl group at δ 2.34 (J = 1.5 Hz), multiplets for the methylene hydrogens at δ 4.70 and 5.02, and a multiplet for the ring olefinic hydrogen at δ 6.86. The ^{13}C NMR spectrum consisted of six peaks with appropriate chemical shifts. The IR spectrum showed an intense absorption at 1779 cm^{-1} which agrees very well with the carbonyl absorption reported for **2** (1783 cm^{-1}).[2]



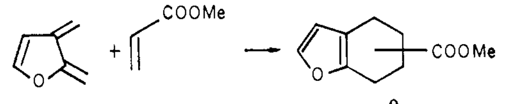
5

7
21%

8
24%

The structure of dimer **8** was also determined by its spectral properties. The ^{1}H NMR spectrum exhibited four-proton singlets at δ 2.78 and 3.04 and two-proton doublets for the furan hydrogens at δ 6.06 (J = 2 Hz) and 7.16 (J = 2 Hz). The ^{13}C NMR spectrum showed six signals, as required by the symmetry of **8**, with appropriate chemical shifts.

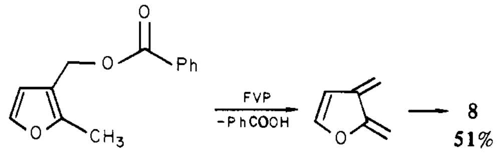
If methyl acrylate is added to a solution of the cold pyrolysis products of **5** prior to warming, a mixture of the Diels–Alder adducts (**9**) is obtained along with **7** and benzoic acid. This observation indicates that **6** is the primary pyrolysis product which dimerizes to **8** upon warming.



6

9

A consideration of the mechanism proposed for the conversion of **1** to **2** suggested that the pyrolysis of 2-methyl-3-furylmethyl benzoate (**10**) would generate **6** in the absence of **7**. The pyrolysis of **10** at 640 °C and 10^{-4} Torr gave a 51% yield of dimer **8**, along with benzoic acid and a large amount of polymeric material. It was also observed that **6** could be trapped with methyl acrylate



10

6

---

[1] (a) Based on work by T.J.C. in partial fulfillment of the requirements for the Ph.D. degree at Iowa State University; (b) National Science Foundation undergraduate research participant, summer 1974.

[2] (a) Trahanovsky, W. S.; Park, M.-G. *J. Am. Chem. Soc.* **1973**, *95*, 5412. (b) *J. Org. Chem.* **1974**, *39*, 1448.

[3] Trahanovsky, W. S.; Alexander, D. L. *J. Am. Chem. Soc.* **1979**, *101*, 142.

[4] For leading references see: McCullough, J. J. *Acc. Chem. Res.* **1980**, *13*, 270.

0002-7863/81/1503-6691$01.25/0

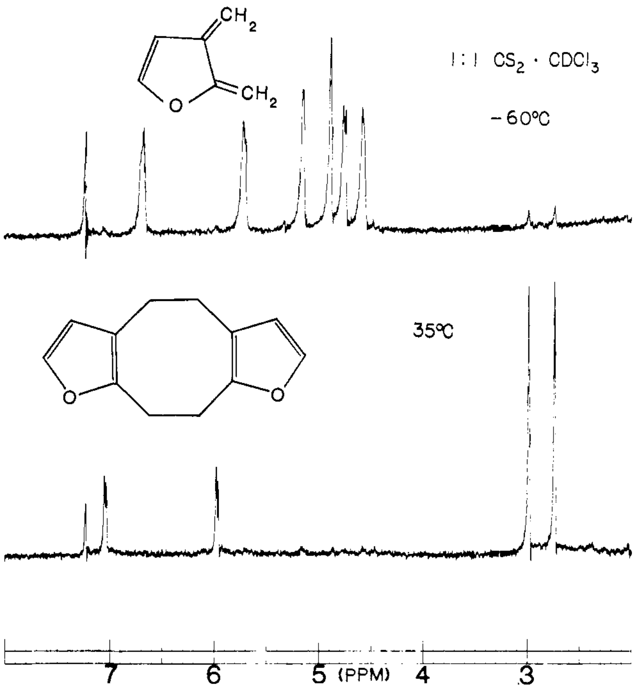
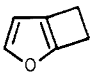


Figure 1. ^{1}H NMR spectra of the pyrolysis products of **10** at -60 °C (top) and at 35 °C (bottom) in 1:1 CS$_2$-CDCl$_3$ (δ 7.2 peak is due to CHCl$_3$).

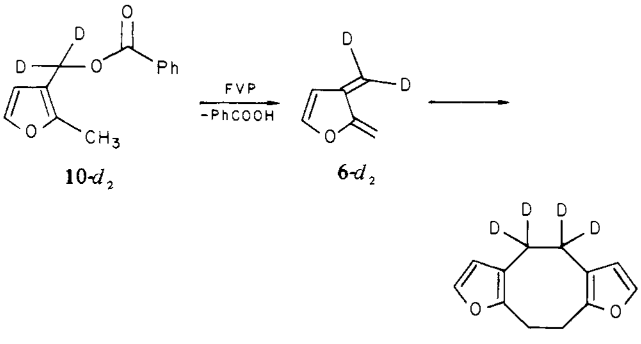
to form the same Diels-Alder adducts (**9**) that were derived from the pyrolysis products of **5**.

Further proof that **6** is a primary pyrolysis product of **5** and **10** was obtained by recording the ^{1}H and ^{13}C NMR spectra of **6** at -60 °C.[5] In Figure 1, the ^{1}H NMR spectra of the pyrolysis products of **10**, recorded at -60 and 35 °C, are presented. An interesting feature of the spectra is the absence of peaks corresponding to furanocyclobutene (**11**), the closed form of **6**. Apparently the resonance energy of the furan ring in **11** is insufficient to compensate for the strain energy of the four-membered ring. Thus it appears that the open form (**6**) is more stable than **11**.



11

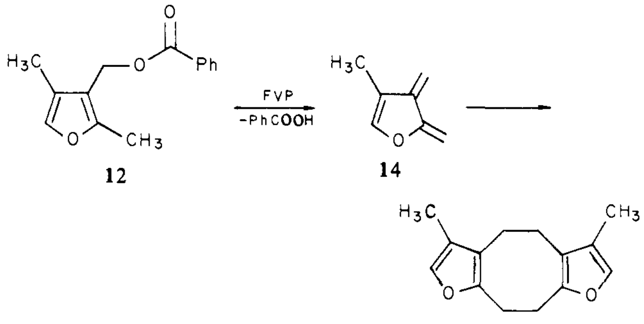
The preparation and pyrolysis of **10**-d_2 was undertaken in order to assign the ^{1}H and ^{13}C NMR signals from **6** and **8**. A mass



10-d_2 **6**-d_2 **8**-d_4

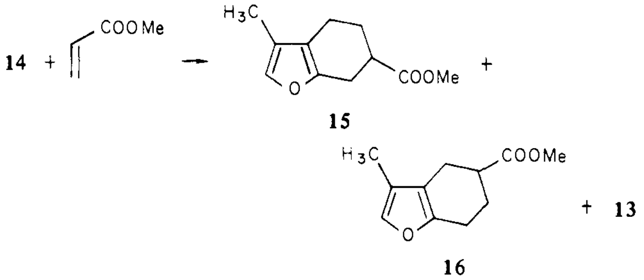
spectral analysis of **10**-d_2 showed greater than 95% D$_2$ incorporation. The ^{1}H and ^{13}C NMR spectra of **6**-d_2 and **8**-d_4 were recorded at -60 and 40 °C, respectively. The ^{1}H NMR spectrum of **6**-d_2 included a doublet at δ 6.73 (J = 1.5 Hz) and a multiplet at δ 5.78 for the ring protons and a doublet at δ 4.85 (J = 1.5 Hz) and a multiplet at δ 4.65 for the 2-methylene protons. The ^{13}C NMR spectrum of **6**-d_2 showed five peaks including one at δ 85.22 for the methylene carbon at the 2 position. A signal at δ 102 for the methylene carbon at the 3 position was not observed.

The high reactivity of **6** as a diene enables its Diels-Alder reactions to serve as a direct method for obtaining the furanocyclohexane ring skeleton. Since a large number of sesquiterpenes contain a furanocyclohexane unit with a β-methyl group on the furan ring,[7] the pyrolysis of 2,4-dimethyl-3-furylmethyl benzoate (**12**) was investigated. The pyrolysis of **12** at 640 °C and 10^{-5} Torr gave a 43% isolated yield of **13**, the head-to-head, [4 + 4] dimer of **14**, along with benzoic acid and a large amount of an off-white polymer. The structures of **13** and **14** were indicated by their ^{1}H and ^{13}C NMR spectra.



12 **14** **13** (43%)

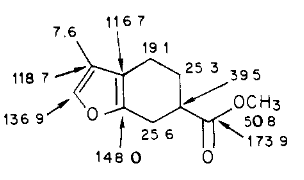
When a large excess of methyl acrylate was added to the product trap, good yields of the Diels-Alder adducts (**15** and **16**)



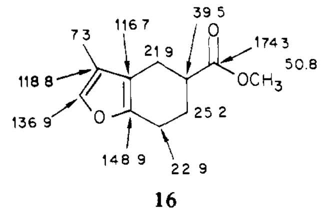
15 **16**

were obtained (64-75%) along with small amounts of dimer (**13**) (2-9%) and substantial amounts of polymer.

The ratio of **15** to **16** was determined by analysis of the ^{13}C NMR spectral data for mixtures of the two isomers. Five of the signals from **15** were sufficiently separated from the corresponding signals of **16** that the areas of the peaks could be used to determine the isomer ratio. An average of four determinations using this method indicated that the ratio of **15** to **16** is 3.0 to 1. The ^{13}C NMR chemical shifts (CS$_2$/CDCl$_3$; δ from Me$_4$Si) are presented below.



15



16

In order to determine the structures of **15** and **16** and to confirm the value for the isomer ratio, the carbomethoxy groups in **15** and **16** were converted to methyl groups. This converted **15** to the commercially available, natural product menthofuran (**17**), while **16** was converted to isomenthofuran (**18**). Since the IR and the

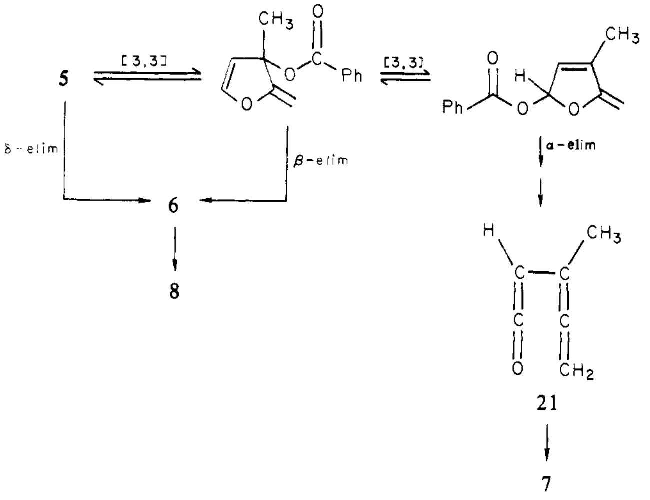
---

(5) The ^{1}H NMR spectrum of **6** can be recorded between -60 and -100 °C. At temperatures below -100 °C, the solubility of **6** diminishes and dimerization occurs rapidly. The enhanced dimerization is probably caused by increased local concentrations of **6**. Perhaps this observation explains the inability of previous workers to obtain NMR spectral data for **6**.[6]

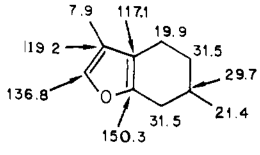
(6) Jullien, J.; Pechine, J. M.; Perez, F.; Piade, J. J. *Tetrahedron Lett.* **1979**, 3079.

(7) For leading references see: Hikino, H.; Konno, C. *Heterocycles* **1976**, *4*, 817.

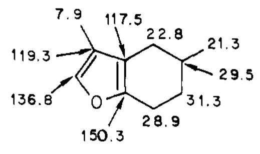
Scheme I



^{1}H NMR spectra of **17** and **18** were virtually superimposable except for some minor peaks in the IR spectra, it was necessary to rely on the ^{13}C NMR spectra to distinguish the isomers. The ^{13}C NMR chemical shifts ($CS_2/CDCl_3$; δ from Me_4Si) of **17** and **18** are presented below.

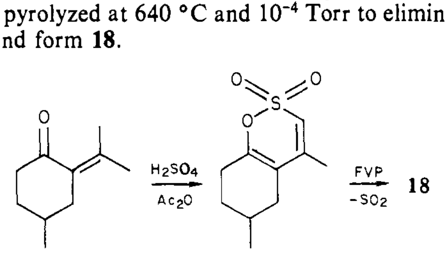


17



18

The ratio of **17** to **18** was determined to be 3.3 to 1 by comparing the areas corresponding to carbon 4 of each isomer (δ 19.9 and 22.8). Isomenthofuran (**18**) was synthesized by an independent route for spectral comparison. 2-Isopropylidine-4-methylcyclohexanone (**19**)[8] was converted to the δ-sultone (**20**) by treatment with sulfuric acid in acetic anhydride.[9] The δ-sultone was then pyrolyzed at 640 °C and 10^{-4} Torr to eliminate sulfur dioxide and form **18**.

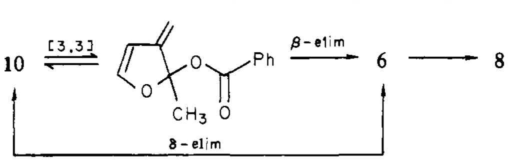


Discussion

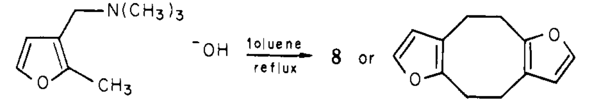
A migration mechanism was previously proposed for the conversion of furfuryl benzoate (**1a**) to methylenecyclobutenone (**2a**).[2] In Scheme I, a set of pathways which account for the formation of the pyrolysis products from **5** is presented.

Structure **6** may be formed either directly from **5** by a δ-elimination of benzoic acid, or by a two-step mechanism involving a [3,3] sigmatropic shift followed by a β-elimination of benzoic acid. Product **7** can be explained by a multistep mechanism involving two [3,3] sigmatropic shifts with subsequent α-elimination of benzoic acid and rearrangement to form 3-methylallenylketene (**21**), which undergoes ring closure to form **7**.

Further support for the migration mechanism was obtained from the study of the pyrolysis products formed from 2-methyl-3-furylmethyl benzoate (**10**). The exclusive formation of **6**, which dimerized to **8** upon warming, can be explained by a direct δ-elimination of benzoic acid or by a two-step mechanism involving a [3,3] shift followed by a β-elimination of benzoic acid.[10]

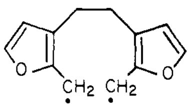


2,3-Dimethylene-2,3-dihydrofuran (**6**) was previously postulated as an intermediate in the liquid-phase pyrolysis of (2-methyl-3-furylmethyl)trimethylammonium hydroxide (**22**).[12] This reaction was reported to give one dimer of **6** possessing either structure **8** or **23**.

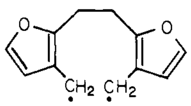


22 **23**

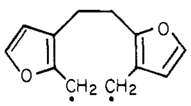
The exclusive formation of dimer **8** from **6** is readily explained by a two-step mechanism involving a diradical intermediate. There are three possible diradical intermediates: **24**, **25**, and **26**. Intermediates **24** and **25** would lead to the formation of dimer **8**, while **26** would lead to the head-to-tail dimer (**23**). Simple resonance considerations suggest that the radical center found in **24** is more stable than that found in **25**, but a stability difference of the two radical centers in favor of either center means that one of the symmetrical diradical intermediates (**24** or **25**) will be more stable than the unsymmetrical intermediate (**26**) which has one of each center. The dimerization mechanism is analogous to that proposed for the dimerization of *o*-xylylene.[13]



24



25



26

Experimental Section

Methods and Materials. The pyrolysis apparatus has been previously described.[14] ^{1}H NMR spectra were recorded on Varian A-60, HA-100, or Hitachi Perkin-Elmer R-20B spectrometers. ^{13}C NMR spectra were recorded on a Bruker HX-90 or a JEOL FX-90Q spectrometer. Chemical shifts are reported in parts per million (δ) from Me_4Si. Infrared spectra were measured with a Beckman 4250 spectrophotometer. High resolution mass spectra were measured with an Associated Electronics Industries MS-902 instrument at 70 eV. Gas chromatography/mass spectral data (GC/MS) were recorded using a Finnigan 4000 instrument with an INCOS 2300 data system. Melting points were determined with a Thomas-Hoover apparatus and are uncorrected.

Menthofuran was purchased from Eastman Organic Chemicals. 3-Methylfurfuryl alcohol[15] was prepared by the lithium aluminum hydride ($LiAlH_4$) reduction of methyl 3-methyl-2-furoate.[16] 2-Methyl-3-furylmethyl alcohol[12] was prepared by the $LiAlH_4$ reduction of ethyl 2-methyl-3-furoate.[12] 2-Isopropylidene-4-methylcyclohexanone (**19**) was prepared from 4-methylcyclohexanone using the method of Russell and co-workers.[8]

---

(8) Russell, G. A.; Jawdosiuk, M.; Ros, F. *J. Am. Chem. Soc.* **1979**, *101*, 3378.

(9) (a) Treibs, W. *Ber.* **1937**, *70*, 85. (b) Pallaud, R.; Berna, J. *Ind. Parfum.* **1953**, *8*, 154. (c) Morel, Th.; Verkade, P. E. *Recl. Trav. Chim. Pays-Bas* **1951**, *70*, 35; **1948**, *67*, 539; **1949**, *68*, 619.

(10) Under comparable conditions *o*-methylbenzyl carboxylates, the benzene analogues, also fragment giving as major products the carboxylic acid and benzocyclobutene, presumably formed from *o*-quinodimethane.[11]

(11) Trahanovsky, W. S.; Morello, M. J. "Abstracts of Papers", 178th National Meeting of the American Chemical Society, Washington, D.C., Sept 1979; American Chemical Society: Washington, D.C., 1979; PETR 46.

(12) Winberg, H. E.; Fawcett, F. S.; Mochel, W. E.; Theobald, C. W. *J. Am. Chem. Soc.* **1960**, *82*, 1428.

(13) Errede, L. A. *J. Am. Chem. Soc.* **1961**, *83*, 949.

(14) Trahanovsky, W. S.; Ong, C. C.; Pataky, J. G.; Weitl, F. L.; Mullen, P. W.; Clardy, J. C.; Hansen, R. S. *J. Org. Chem.* **1971**, *36*, 3575.

(15) Elliot, M.; Janes, N. F.; Pearson, B. C. *Pestic. Sci.* **1971**, *2*, 243.

(16) Burness, D. M.; "Organic Syntheses", Collect. Vol. IV; Wiley: New York, 1963; p 649.

3-Methylfurfuryl Benzoate (5). A solution of 20.10 g of benzoyl chloride (143 mmol) in 50 mL of ether was added over a 15-min period to a stirred solution containing 16.00 g of 3-methylfurfuryl alcohol (143 mmol)[15] and 11.29 g of pyridine (143 mmol) in 100 mL of ether. The mixture was then stirred at room temperature for 4 h. After the addition of 75 mL of water, the layers were separated and the aqueous portion was extracted twice with 25 mL of ether. The combined ether layers were washed successively with 1 M hydrochloric acid (3 × 50 mL), saturated sodium bicarbonate (2 × 50 mL), and saturated sodium chloride (3 × 50 mL). After drying ($MgSO_4$) and removal of the solvent, the crude product was purified by vacuum distillation to yield 29.01 g (134 mmol; 93%) of **5**: bp 110 °C (0.65 mm); IR (CCl_4) 1724, 1268, 1095 cm^{-1}; ^1H NMR (CCl_4) δ 8.25–7.9 (m, 2 H), 7.7–7.1 (m, 4 H), 6.17 (d, J = 2 Hz, 1 H), 5.23 (s, 2 H), 2.1 (s, 3 H); high resolution mass spectrum, calcd for $C_{13}H_{12}O_3$ 216.0786, measured 216.0779.

2-Methyl-3-furylmethyl benzoate (10). A solution of benzoyl chloride (80.7 mmol) in 50 mL of ether (dried over $LiAlH_4$) was added dropwise to a stirred solution of 2-methyl-3-furylmethyl alcohol (80.0 mmol) and triethylamine (96 mmol) in 100 mL of dry ether. After mixture was stirred for 10 h at room temperature, 100 mL of water was added and the products were isolated using the method described for the preparation of **5**. A vacuum distillation of the crude product yielded 15.9 g (73.5 mmol; 92%) of **10**: bp 88 °C (0.01 mm); IR (thin film) 1720, 1625, 1600, 1515, 1270, 925 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.2–7.9 (m, 2 H), 7.7–7.3 (m, 3 H), 7.25 (d, J = 2 Hz, 1 H), 6.41 (d, J = 2 Hz, 1 H), 5.16 (s, 2 H), 2.35 (s, 3 H); high resolution mass spectrum, calcd for $C_{13}H_{12}O_3$ 216.0786, measured 216.0783.

2-Methyl-3-furylmethyl-α,α-d_2 Benzoate (10-d_2). To a stirred slurry of 1.498 g (35.7 mmol) of lithium aluminum deuteride in 10 mL of dry ether ($LiAlH_4$) at 0 °C was slowly added a solution of 5.304 g (34.4 mmol) of ethyl 2-methyl-3-furoate[12] in 15 mL of dry ether. The mixture was stirred at room temperature for 6 h and a standard workup[17] gave 3.47 g (30.4 mmol; 88.4%) of 2-methyl-3-furylmethyl-α,α-d_2 alcohol: IR (thin film) 3330 (br), 2260–2050, 1635, 1520, 1415, 1228, 1075, 1025 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.16 (d, J = 2 Hz, 1 H), 6.28 (d, J = 2 Hz, 1 H), 3.33 (s, 1 H), 2.21 (s, 3 H); high resolution mass spectrum, calcd for $C_6H_6D_2O_2$ 114.06499, measured 114.06521. Without further purification 3.41 g (29.9 mmol) of the alcohol was converted to **10**-d_2 using the procedure described for the synthesis of **10**. The benzoate was purified by column chromatography on silica gel (2% ether in hexanes) followed by distillation yielding 5.9 g (27 mmol; 90.4%) of **10**-d_2: IR (thin film) 2280–2100, 1720, 1605, 1520, 1175, 1025, 1010 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.24–7.27 (m, 5 H), 7.21 (d, J = 2 Hz, 1 H), 6.37 (d, J = 2 Hz, 1 H), 2.35 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 166.53, 151.04, 140.58, 132.89, 130.34, 129.64, 128.34, 114.52, 111.65, 11.65; high resolution mass spectrum, calcd for $C_{13}H_{10}D_2O_3$ 218.09120, measured 218.09071. Mass spectral analysis at 20 eV showed that the benzoate was >95% d_2.

2,4-Dimethyl-3-furylmethyl Benzoate (12). To a stirred slurry of 6.3 g (166 mmol) of $LiAlH_4$ in 120 mL of dry ether ($LiAlH_4$) at 0 °C was slowly added a solution of 28.10 g (167 mmol) of ethyl 2,4-dimethyl-3-furoate.[18] The mixture was stirred at room temperature for 5 h and a standard workup[17] gave 19.7 g (156 mmol; 94%) of 2,4-dimethyl-3-furylmethyl alcohol:[19] IR (thin film) 3330 (br), 1635, 1565, 1275, 1115, 900 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.98 (m, 1 H), 4.3 (s, 2 H), 3.25 (s, 2 H), 2.2 (s, 3 H), 1.95 (d, J = 1.5 Hz, 3 H). Without further purification, the alcohol was converted to benzoate **12** in 98% yield using the method previously described. Purification by chromatography on silica gel (1% in ether in hexanes) followed by distillation yielded 32.5 g (141 mmol; 85% isolated yield from ethyl 2,4-dimethyl-3-furoate) of pure **12**: IR (thin film) 1715, 1598, 1575, 1450, 1265, 1170, 1020 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.2–7.9 (m, 2 H), 7.7–7.2 (m, 3 H), 7.07 (m, 1 H), 5.15 (s, 2 H), 2.31 (s, 3 H), 2.02 (d, J = 1.5 Hz, 3 H); ^{13}C NMR ($CDCl_3/CS_2$) δ 166.2, 151.5, 137.3, 132.7, 130.6, 129.6, 128.3, 120.7, 115.3, 57.3, 11.8, 8.2; high resolution mass spectrum, calcd for $C_{14}H_{14}O_3$ 230.094298, measured 230.09448.

General Pyrolysis Procedure. The furnace was maintained at temperatures ranging between 600 and 640 °C. A sample of the furylmethyl ester in a Pyrex boat was placed into the sample chamber and the system was evacuated to ca. 10^{-4} Torr. The sample chamber was heated to ca. 70 °C during the pyrolysis. A condenser cooled to ca. −20 °C was inserted between the furnace and the liquid-nitrogen-cooled trap to collect the benzoic acid formed as a byproduct. During the pyrolyses carbon disulfide and in some cases a reagent was deposited onto the trap through a side arm. Upon completion of the reaction nitrogen was introduced into the system and the trap was warmed to −78 °C. Carbon disulfide or a reagent solution at −78 °C was used to rinse the walls of the trap and then the temperature was slowly raised to room temperature. The product solution was dried (Na_2CO_3), filtered, and concentrated.

Pyrolysis of 3-Methylfurfuryl Benzoate (5). A 2.0 g (9.25 mmol) quantity of 3-methylfurfuryl benzoate (**5**) was pyrolyzed at 630 °C in the normal manner. A quantitative ^1H NMR analysis of the pyrolysate using a dibromoethane standard showed the presence of 3-methyl-4-methylenecyclobutenone (**7**) in 21% yield and dimer **8** in 24% yield. Thick layer chromatography on silica gel plates (2000 μ) using two elutions with 20% ethyl acetate in hexanes afforded two major bands. The upper band consisted of 0.313 g (1.67 mmol; 18%) of 4*H*,5*H*,9*H*,10*H*-cycloocta[1,2-*b*:6,5-*b'*]difuran (**8**): mp 49–52 °C (lit.[10] 54–55 °C); IR ($CHCl_3$) 1610, 1500, 1436, 1040, 895 cm^{-1}; ^1H NMR (CS_2) 7.16 (d, J = 2 Hz, 2 H), 6.06 (d, J = 2 Hz, 2 H), 3.04 (s, 4 H), 2.78 (s, 4 H); high resolution mass spectrum, calcd for $C_{12}H_{12}O_2$ 188.08373, measured 188.08359. The lower band consisted of 3-methyl-4-methylenecyclobutenone (**7**) (0.139 g; 1.48 mmol; 16%): IR (CS_2) 1779 cm^{-1}; ^1H NMR (CS_2) δ 6.86 (m, 1 H), 5.02 (m, 1 H), 4.70 (m, 1 H), 2.34 (d, J = 1.5 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 187.68, 186.18, 159.65, 149.70, 95.34, 13.98; GC/MS (70 eV) m/e (% base peak) 96.00 (0.04), 95.00 (2.54), 94.00 (42.38), 66.00 (85.28), 65.00 (55.38), 63.00 (12.95), 51.00 (39.44), 50 (27.27), 39.00 (100.00), 38.00 (23.11).

Pyrolysis of 2-Methyl-3-furylmethyl Benzoate (10). A 1.64-g quantity (7.6 mmol) of **10** was pyrolyzed at 630 °C in the normal manner. The pyrolysate was collected in carbon disulfide, dried (Na_2CO_3), and concentrated. GC and ^1H NMR analyses of the crude product mixture indicated that dimer **8** was the only major product formed, along with benzoic acid. The oily product mixture was purified by sublimation at 0.15 mm with a bath temperature between 90 and 115 °C, yielding 0.364 g (1.93 mmol; 51%) of a white powder, 4*H*,5*H*,9*H*,10*H*-cycloocta[1,2-*b*:6,5-*b'*]difuran (**8**): mp 53–53.5 °C (lit.[12] 54–55 °C); IR ($CHCl_3$) 1615, 1510, 1440, 1045, 892 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.12 (d, J = 2 Hz, 2 H), 6.05 (d, J = 2 Hz, 2 H), 3.00 (s, 4 H), 2.74 (s, 4 H); ^{13}C NMR ($CDCl_3$) δ (coupling observed in gated decoupled spectrum) 149.85 (s), 139.72 (d, J = 199.6 Hz), 117.94 (s), 113.44 (d, J = 172.1 Hz), 25.79 (t, J = 126.3 Hz), 24.87 (t, J = 127.6 Hz); high resolution mass spectrum, calcd for $C_{12}H_{12}O_2$ 188.08373, measured 188.08368.

2,3-Dimethylene-2,3-dihydrofuran (6). A 0.3837-g (1.77 mmol) quantity of 2-methyl-3-furylmethyl benzoate (**10**) was pyrolyzed at 635 °C in the normal manner. During the pyrolysis, 2 mL of 1:1 $CS_2/CDCl_3$ was deposited into the product trap. After the reaction was finished, the trap was warmed to −78 °C and 2 mL of 1:1 $CS_2/CDCl_3$ at −78 °C was used to rinse the walls of the trap. After transferring some of the product solution to NMR tubes at −78 °C, the ^1H and ^{13}C NMR spectra were recorded, indicating the presence of **6**: ^1H NMR (1:1 $CS_2/CDCl_3$, −60 °C) δ 6.68 (m, 1 H), 5.73 (m, 1 H), 5.17 (m, 1 H), 4.90 (s, 1 H), 4.75 (d, J = 1.1 Hz, 1 H), 4.58 (m, 1 H); ^{13}C NMR (1:1 $CS_2/CDCl_3$, −60 °C) δ 157.62 (s), 148.30 (d, J = 199.6 Hz), 139.63 (s), 107.61 (d, J = 177 Hz), 102.09 (t, J = 161.7 Hz), 85.08 (t, J = 162.4 Hz). Upon warming above −40 °C **6** dimerized forming **8**. Quantitative ^1H NMR analysis using a dichloroethane standard indicated that 98.5% of **6** was converted to **8** upon warming to room temperature.

Pyrolysis of 2-Methyl-3-furylmethyl-α,α-d_2 Benzoate (10-d_2). A 0.431-g (2.0 mmol) quantity of (**10**-d_2) was pyrolyzed in the normal manner. The pyrolysate was collected in 4 mL of 1:2 $CS_2/CDCl_3$ and NMR spectral data were recorded at low temperature for **6**-d_2: ^1H NMR (1:2 $CS_2/CDCl_3$, −60 °C) δ 6.73 (d, J = 1.5 Hz, 1 H), 5.78 (m, 1 H), 4.85 (d, J = 1.5 Hz, 1 H), 4.65 (m, 1 H); ^{13}C NMR (1:2 $CS_2/CDCl_3$, −60 °C) δ 157.86, 148.55, 139.55, 107.75, 85.22. Upon warming to room temperature **6**-d_2 was cleanly converted to **8**-d_4: ^1H NMR (1:2 $CS_2/CDCl_3$) δ 7.05 (d, J = 2 Hz, 2 H), 6.00 (d, J = 2 Hz, 2 H), 3.00 (s, 4 H); ^{13}C NMR (1:2 $CS_2/CDCl_3$) δ 149.52, 139.55, 113.33, 25.90. The signal for the ring carbons attached to the CD_2 moieties were not observed after 25 000 scans (pulse width = 4.0 μs). ^1H NMR spectral analysis of **8**-d_4 showed no evidence for any deuterated species other than **8**-d_4.

Diels–Alder Reaction of 6 with Methyl Acrylate. A 0.2708-g (1.25 mmol) quantity of **10** was pyrolyzed at 620 °C. A solution of 10 mL of methyl acrylate in 10 mL of carbon disulfide was deposited into the trap during the pyrolysis. After the reaction was finished, the trap was warmed to −30 °C and stirred for 2 h. The product mixture was then warmed to room temperature, dried (Na_2CO_3), and concentrated. Purification with a molecular-distillation apparatus yielded 0.1670 g (0.93 mmol, 74.14%) of the Diels–Alder adducts **9**: IR ($CHCl_3$), 1735, 1610, 1510, 1445, 1255, 1200, 1175, 1108, 860 cm^{-1}; ^1H NMR (CS_2) 7.09 (d,

---

[17] Fieser, L. F.; Fieser, M., "Reagents for Organic Synthesis"; Wiley: New York, 1967; Vol. 1, p 584.

[18] (a) Alexander, E. R.; Baldwin, S. *J. Am. Chem. Soc.* **1951**, *73*, 356. (b) Feist, E. *Ber.* **1902**, *35*, 1537, 1545. (c) Benary, E. *Ibid.* **1911**, *44*, 489, 493. (d) Howes, P. D.; Stirling, C. J. M. *Org. Syn.* **1973**, *53*, 1.

[19] Novitskii, K. Y.; Khachaturova, G. T.; Bairamova, N. E.; Yur'ev, Y. K. *Khim. Geterotsikl. Soedin.* **1966**, 835.

J = 2 Hz, 1 H), 6.02 (d, *J* = 2 Hz, 1 H), 3.59 (s, 3 H), 2.92–1.55 (m, 7 H); high resolution mass spectrum, calcd for $C_{10}H_{12}O_3$ 180.078648, measured 180.078683.

Pyrolysis of 2,4-Dimethyl-3-furylmethyl Benzoate (12). A 3.01-g quantity (13.1 mmol) of **12** was pyrolyzed at 620 °C in the normal manner. The pyrolysate was collected in 25 mL of carbon disulfide, dried (Na_2CO_3), and concentrated, yielding a clear, viscous liquid. Column chromatography on silica gel (hexanes as eluant) gave 0.70 g (3.2 mmol; 49.6%) of 3,6-dimethyl-4*H*,5*H*,9*H*,10*H*-cycloocta[1,2-*b*:6,5-*b*′]difuran (**13**): IR ($CHCl_3$) 1630, 1565, 1440, 1382, 1132, 1077, 860 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.02 (m, 2 H), 3.07 (s, 4 H), 2.73 (s, 4 H), 1.92 (d, *J* = 1.54 Hz, 6 H); ^{13}C NMR (1:1 $CS_2/CDCl_3$) 150.06 (s), 136.57 (d, *J* = 198 Hz), 120.97 (s), 118.32 (s), 26.22 (t, *J* = 127 Hz), 22.43 (t, *J* = 128 Hz), 8.18 (q, *J* = 127 Hz); high resolution mass spectrum, calcd for $C_{14}H_{16}O_2$ 216.11503, measured 216.11543.

4-Methyl-2,3-dimethylene-2,3-dihydrofuran (14). A 0.41-g quantity (1.8 mmol) of **12** was pyrolyzed at 620 °C and the pyrolysate was isolated using the procedure previously described for **6**. The low-temperature ^{1}H and ^{13}C NMR spectra indicated the presence of **14**: ^{u}H NMR (CS_2, −60 °C) δ 6.61 (m, 1 H), 5.27 (m, 1 H), 4.84 (m, 2 H), 4.65 (m, 1 H), 1.89 (d, *J* = 1.5 Hz, 3 H); ^{13}C NMR (1:1 $CS_2/CDCl_3$, −72 °C) δ 158.41, 144.38, 141.99, 115.12, 99.95, 85.00, 7.86. Upon warming above −30 °C **14** dimerizes cleanly to **13**.

Diels–Alder Reaction of 14 with Methyl Acrylate. A 2.38-g quantity (10.3 mmol) of 2,4-dimethyl-3-furylmethyl benzoate (**12**) was pyrolyzed at 640 °C. The pyrolysate was collected in 40 mL of a 1:1 mixture of methyl acrylate in carbon disulfide at −78 °C. The product mixture was then slowly warmed to room temperature, dried (Na_2CO_3), and concentrated. Chromatography on silica gel (5% ether in hexanes) yielded 1.57 g (8.06 mmol; 78%) of the Diels–Alder adducts (**15** and **16**) separated from 0.0414 g (0.19 mmol; 3.7%) of dimer **13**. For **15** and **16**: IR (thin film) 1735, 1635, 1568, 1187, 1160, 1035, 895 cm^{-1}; ^{1}H NMR (CS_2) δ 6.94 (m, 1 H), 3.62 (s, 3 H), 2.8–1.5 (m, 10 H); high resolution mass spectrum, calcd for $C_{11}H_{14}O_3$ 194.094298, measured 194.09435.

Preparation of a Mixture of Menthofuran (17) and Isomenthofuran (18). To a stirred slurry of $LiAlH_4$ (0.2 g; 5.3 mmol) in 10 mL of dry ether ($LiAlH_4$) at 0 °C was added a solution of **15** and **16** (1.00 g; 5.2 mmol) in 15 mL of dry ether. After the mixture was stirred for 5 h at room temperature, a standard workup[17] gave 0.79 g (4.8 mmol; 92%) of a mixture of the isomeric alcohols: IR (thin film) 3370 (br), 1655, 1570, 1422, 1045, 870 cm^{-1}; ^{1}H NMR (CS_2) δ 6.82 (m, 1 H), 3.92 (s, 1 H), 3.40 (d, *J* = 5.5 Hz, 2 H), 2.55–1.0 (m, 10 H). Without further purification the isomeric alcohols were converted to the corresponding mesylates using a standard procedure.[20] For the mesylates: IR (thin film) 1645, 1560, 1425, 1355, 1175, 885, 735 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.1 (m, 1 H), 4.2 (distorted d, *J* = 5.5 Hz, 2 H), 3.04 (s, 3 H), 2.9–1.0 (m, 10 H). Because of their instability the mesylates were immediately reduced without further purification. A solution of the mesylates in 5 mL of dry THF ($LiAlH_4$) was slowly added to a slurry of $LiAlH_4$ (0.5 g; 13 mmol) in 10 mL of THF at 0 °C. After the mixture was refluxed for 26 h, 50 mL of ether was added and a standard workup[17] was employed yielding 0.56 g (3.8 mmol) of crude product. A short-path distillation gave 0.25 g (1.7 mmol, 35%) of an inseparable mixture of menthofuran (**17**) and isomenthofuran (**18**): bp (bath temp) 34–49 °C (0.05 mm); IR (thin film) 1645, 1565, 1418, 1100, 1090, 1020, 900, 860, 710, 695 cm^{-1}; ^{1}H NMR (CS_2) δ 6.8 (m, 1 H), 3.0–0.8 (m, 7 H), 1.93 (d, *J* = 1.5 Hz, 3 H), 1.05 (distorted d, *J* = 5.5 Hz, 3 H); high resolution mass spectrum, calcd for $C_{10}H_{14}O$ 150.10447, measured 150.10425. A ^{13}C NMR analysis of the product mixture indicated that the ratio of **17** to **18** was 3.3 to 1 (average of two runs).

Menthofuran (17) (3,6-Dimethyl-4,5,6,7-tetrahydrobenzofuran). A commercial sample was purified by distillation to give an analytical sample of **17**: bp 26–27 °C (0.1 mm); IR (thin film) 1645, 1565, 1422, 1105, 1095, 1025, 905, 865, 695 cm^{-1}; ^{1}H NMR (CS_2) δ 6.83 (m, 1 H), 3.0–0.8 (m, 7 H), 1.84 (d, *J* = 1.5 Hz, 2 H), 1.0 (distorted d, *J* = 5.5 Hz, 3 H); ^{13}C NMR (1:1 $CS_2/CDCl_3$) δ 150.3 (s), 136.8 (d, *J* = 198 Hz), 119.2 (s), 117.1 (s), 31.5 (t, *J* = 127.6 Hz), 29.7 (d), 21.4 (q, *J* = 123.3 Hz), 19.9 (t, *J* = 127 Hz), 7.9 (q, *J* = 126.5 Hz); high resolution mass spectrum, calcd for $C_{10}H_{14}O$ 150.10447, measured 150.10404.

Preparation of Isomenthofuran (18) (2,5-Dimethyl-4,5,6,7-tetrahydrobenzofuran). To a stirred mixture of 2.7 mL of concd sulfuric acid (48.6 mmol) in 10 mL of acetic anhydride (159 mmol) at −2 °C was slowly added 6.87 g (45.2 (mmol) of 2-isopropylidene-4-methylcyclohexanone (**19**).[8] The reddish-brown mixture was maintained at −2 °C for 26 h and then for 4 h at room temperature. After the addition of 5 mL of distilled water the crystals were collected, washed with cold methanol, and dried yielding 3.46 g (16.2 mmol; 36%) of 2-(5′-methylcyclohexen-1′-yl)propen-1,2′-sultone (**20**): IR ($CHCl_3$) 1658, 1580, 1370, 1152 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 6.25 (m, 1 H), 2.8–0.8 (m, 13 H). A 2.47-g (11.5 mmol) quantity of **20** was pyrolyzed at 640 °C and 10^{-4} Torr in the normal manner by heating the sample chamber between 70 and 120 °C. The pyrolysate was dissolved in ether, dried (Na_2CO_3), and concentrated. A short-path distillation gave 1.31 g (8.7 mmol; 75%) of isomenthofuran (**18**): IR (thin film) 1645, 1567, 1415, 1100, 1085, 898, 860, 707 cm^{-1}; ^{1}H NMR (CS_2) δ 6.86 (m, 1 H), 2.95–0.75 (m, 7 H), 1.82 (d, *J* = 1.5 Hz, 3 H), 1.02 (distorted d, *J* = 5.3 Hz, 3 H); ^{13}C NMR (1:1 $CS_2/CDCl_3$) δ 150.3 (s), 136.8 (d, *J* = 198 Hz), 119.3 (s), 117.5 (s), 31.3 (t, *J* = 127 Hz), 29.5 (d, *J* = 123 Hz), 28.9 (t, *J* $\cong$ 133 Hz), 22.8 (t, *J* = 127 Hz), 21.3 (q, *J* = 125 Hz), 7.9 (q, *J* = 127 Hz); high resolution mass spectrum, calcd for $C_{10}H_{14}O$ 150.10447, measured 150.10424.

Acknowledgment. This work was supported primarily by the U.S. Department of Energy, Office of Basic Energy Sciences, Chemical Sciences Division, Budget Code AK-01-03-021 under Contract W-7405-ENG-82. The Mobil Foundation provided funds for a summer research appointment for T.J.C. We thank Professor Glen A. Russell for providing us with a sample of 2-isopropylidene-4-methylcyclohexanone (**19**). We are also grateful to Professor Thomas A. Spencer for providing us with an IR spectrum of isomenthofuran (**18**) made by an independent route.[21]

---

(20) Crossland, R. K.; Servis, K. L. *J. Org. Chem.* **1970**, *35*, 3195.

(21) Garst, M. E.; Spencer, T. A. *J. Org. Chem.* **1974**, *39*, 584.