according to the procedure described above, starting from anhydride (0.64 mmol) and elemental chlorine (0.0681 g, 0.96 mmol) in methylene chloride (3 mL). At −80 °C ^{31}P NMR analysis revealed the presence of **8a**,**b**. ^{31}P NMR chemical shifts are given in Table III.

Acknowledgment. This research was supported by the Polish Academy of Sciences (Project MR.I.12.).

Registry No. (*R*)-(+)-**1** (R = Bu-*t*, R^1 = Ph; R^3 = H), 55705-77-6; (*S*)-(−)-**1** (R = Bu-*t*, R^1 = Ph, R^3 = H), 54100-47-9; (*R*)-(+)-**4**, 51584-30-6; (*S*)-(−)-**4**, 51584-29-3; (*R*,*S*)-**4**, 76380-86-4; (*R*)-(+)-**5**, 75213-02-4; (*S*)-(−)-**5**, 75213-01-3; **7** (isomer 1), 104092-20-8; **7** (isomer 2), 104153-59-5; **8** (isomer 1), 104092-21-9; **8** (isomer 2), 104154-51-0; (*R*)-(+)-**11**, 33586-26-4; **12**, 29949-69-7; **13**, 4923-86-8; **14**, 104092-22-0; **15**, 104114-64-9; **16**, 104092-24-2; **17**, 104092-25-3; **18**, 104114-65-0; **19**, 62839-84-3.

Preparation of 2,3-Dimethylene-2,3-dihydrobenzofuran by the Flash Vacuum Pyrolysis of (2-Methyl-3-benzofuryl)methyl Benzoate[1]

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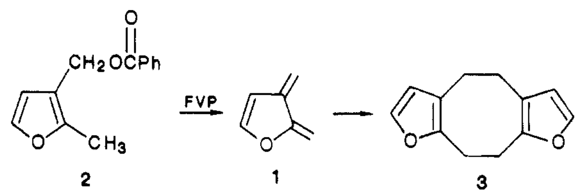
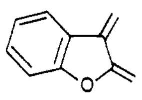
Received April 3, 1986

Pyrolysis of (2-methyl-3-benzofuryl)methyl benzoate (**7**) gives a 30% yield of two dimers of 2,3-dimethylene-2,3-dihydrobenzofuran (**4**), a [4 + 2] dimer (**12**) and a [4 + 4] dimer (**13**), in a ratio of 4.1 to 1. It is shown, by low-temperature ^{1}H NMR spectroscopy, that the primary pyrolysis product from **7** is **4**, which forms **12** and **13** upon warming. The structure of the [4 + 2] dimer **12** is confirmed by a deuterium-labeling experiment. Compound **4** can be trapped with methyl acrylate to form a 3.0 to 1 ratio of two Diels–Alder adducts.

During the past few years, 2,3-dimethylene-2,3-dihydrofuran (**1**), the furan analogue of *o*-xylylene,[2] has been actively investigated by our research group.[3,4] Compound **1** can be conveniently prepared by the flash vaccum pyrolysis (FVP) of (2-methyl-3-furyl)methyl benzoate (**2**). Compound **1** in solution at temperatures above −30 °C dimerizes rapidly and quantitatively to the head-to-head [4 + 4] dimer **3**.[3,4]



As part of our study of quinodimethanes, we selected for study the benzo analogue of **1**, 2,3-dimethylene-2,3-dihydrobenzofuran (**4**). We anticipated that **4**, as a result of the aromaticity of its benzene ring, would be less reactive than **1** and hence more amenable to study. Also, **1** and some substituted 2,3-dimethylene-2,3-dihydrofurans are the only known *o*-quinodimethanes that favor [4 + 4] dimerization over [4 + 2] dimerization and we wished to probe the effects of the fused benzene ring on the mode of dimerization of the furan *o*-quinodimethane system.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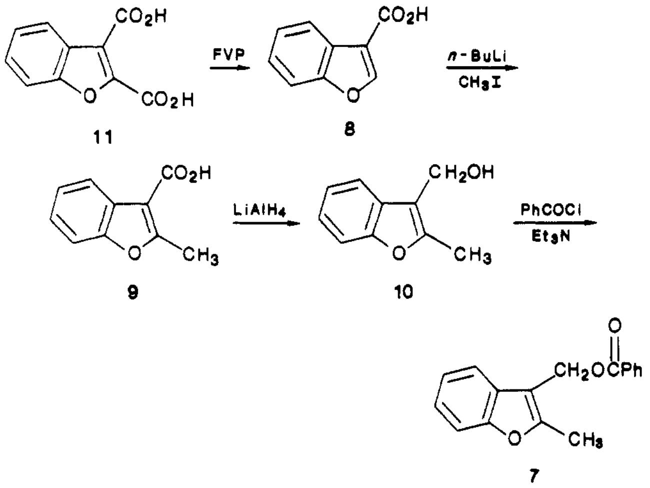
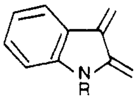
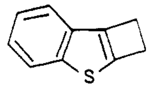
Scheme I



Prior to our work, **4** had not been prepared although indole-2,3-quinodimethanes **5** have been reported[5-18] and


5


6

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[1] Based on work by C. H. Chou in partial fulfillment of the requirements for the Ph.D. Degree at Iowa State University.

(2) For leading references, see: McCullough, J. J. *Acc. Chem. Res.* **1980**, *13*, 270.

(3) Trahanovsky, W. S.; Cassady, T. J.; Woods, T. L. *J. Am. Chem. Soc.* **1981**, *103*, 6691.

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(5) Bergman, J.; Carlsson, R. *Tetrahedron Lett.* **1977**, 4663.

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0022-3263/86/1951-4208$01.50/0

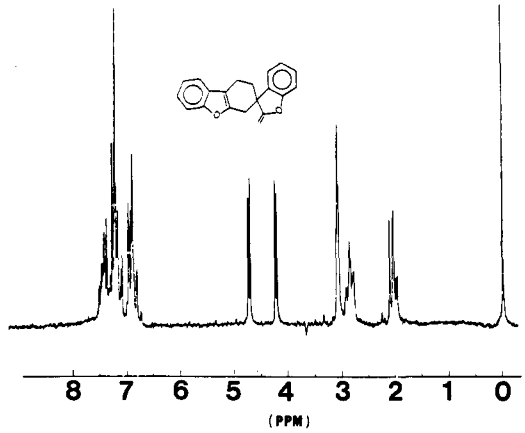
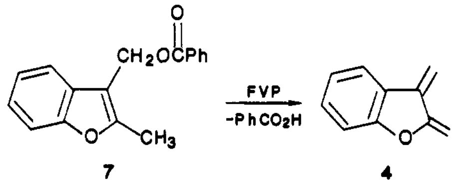


Figure 1. ^1H NMR spectrum of the [4 + 2] dimer **12** in $CDCl_3$.

the closed form of the sulfur analogue, **6**, has been prepared.[19,20] We have developed a synthesis of **4** based on the FVP of (2-methyl-3-benzofuryl)methyl benzoate (**7**)



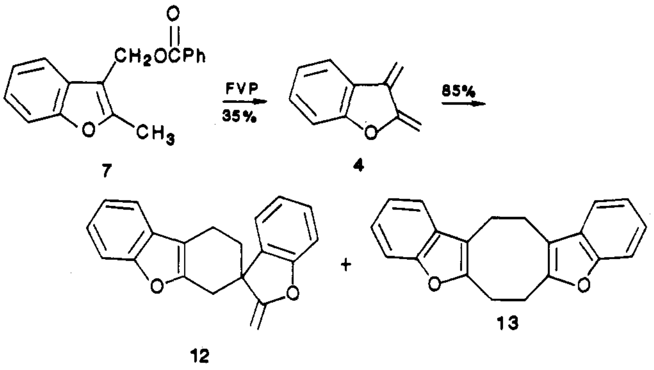
and have studied the dimerization and a Diels–Alder reaction of **4**. The results of this investigation are presented herein.

Results

(2-Methyl-3-benzofuryl)methyl benzoate (**7**) used in this work was prepared by the methylation of 3-benzofurancarboxylic acid (**8**), as indicated in Scheme I, to give 2-methyl-3-benzofurancarboxylic acid (**9**) followed by lithium aluminum hydride reduction to the corresponding alcohol (**10**) which was esterified with benzoyl chloride in the presence of triethylamine. Acid **8** was prepared by a known sequence of reactions which starts from ethyl phenoxyacetate and involves the decarboxylation of diacid **11**.[21] Decarboxylation of **11** was carried out by FVP at 700 °C and ca. 10^{-4} torr to give acid **8** in greater than 80% yield.[22]

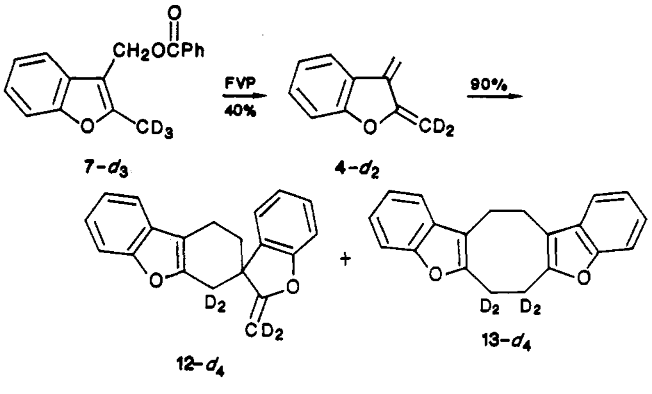
The FVP of **7** was performed using the method previously reported[23] at temperatures 620–640 °C and ca. 10^{-4} torr. A white band of products was produced in the cold trap at −196 °C. A 1:1 mixture of carbon disulfide and deuterated chloroform was added to the trap and the product mixture was allowed to warm slowly to −78 °C. After the product was transferred to an NMR tube at −78 °C, the ^1H NMR spectrum was recorded at −60 °C. This spectrum revealed the presence of 2,3-dimethylene-2,3-dihydrobenzofuran (**4**). Quantitative ^1H NMR analysis, using dibromoethane as the standard, indicated that a 35% yield of **4** was obtained from the FVP of **7**. Compound **4** is stable in $CS_2/CDCl_3$ at −60 °C, but at room temperature it dimerizes slowly to give more than one dimer.

A gas chromatograph/mass spectral (GC/MS) analysis of the dimerization products of **4** indicated that two major dimers in a ratio of 4.1 to 1 were formed in 85% yield. These two dimers were separated by thin-layer chromatography (TLC). The major products from **4** is the [4 + 2] spiro dimer **12**, whereas the minor one is head-to-head [4 + 4] dimer **13**. The ^1H NMR spectrum of **12** is presented in Figure 1. Unlike the [4 + 4] dimer **13**, the [4 + 2] dimer **12** is not a stable compound and it decomposes rapidly during the course of the TLC separation. However, it stays intact in $CS_2/CDCl_3$ solution under nitrogen in the freezer for several days.



In order to confirm the structure of **12** and to assign the ^1H NMR signals from **4**, **12**, and **13**, [2-(trideuteriomethyl)-3-benzofuryl]methyl benzoate (**7**-d_3) was prepared and pyrolyzed. Compound **7**-d_3 was prepared by the procedure outlined in Scheme I using CD_3I instead of CH_3I.

The pyrolysis of **7**-d_3 in the normal fashion gave **4**-d_2 in 40% yield. Dimerization of **4**-d_2 at room temperature in 90% total yield gave a 4.4 to 1 ratio (by GC analysis) of [4 + 2] dimer **12**-d_4 to [4 + 4] dimer **13**-d_4.



Dimers **12**-d_4 and **13**-d_4 were separated by TLC. The ^1H NMR spectrum of **12**-d_4 showed no methylene signals at δ 4.75 and 4.25, and no broad singlet at δ 3.1 but did show the multiplets at δ 2.87 and 2.04 which are consistent with two adjacent undeuterated-methylene groups. Thus the structure presented for **12** is confirmed by the ^1H NMR spectrum of **12**-d_4.

The ^1H NMR spectrum of **13**-d_4 was identical with that of **13** except there was no singlet at δ 3.3, a result consistent with the structure assigned to **13**.

When a large excess of methyl acrylate was added to the pyrolysis product trap before warming, a mixture of the Diels–Alder adducts (**14** and **15**) was obtained (30–40%

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(20) Neckers, D. C.; Wagenaar, F. L.; Hauenstein, D.; Jacobson, R. A. *J. Org. Chem.* **1983**, *48*, 1725.

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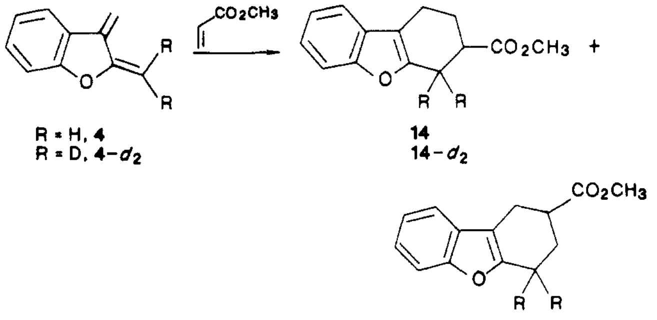
yield) along with small amounts of dimers **12** and **13** (2–5%) and substantial amounts of polymer.



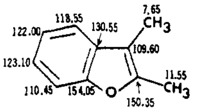
R = H, **4**
R = D, **4**-d_2

14
14-d_2

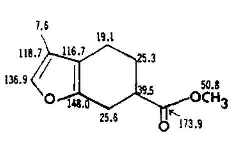
15
15-d_2

Since the ^{1}H NMR spectra of **14** and **15**, and those of **14**-d_2 and **15**-d_2, were virtually superimposable and since repeated attempts to separate the adduct mixtures by GC, TLC, or fractional recrystallization resulted in failure, it was necessary to rely on the ^{13}C NMR spectra to distinguish the isomers.

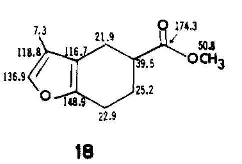
A comparison of the ^{13}C NMR spectral data of the mixture of **14** and **15** to those of 2,3-dimethylbenzofuran (**16**)[24] and of the known Diels–Alder adducts (**17** and **18**) formed between 4-methyl-2,3-dimethylene-2,3-dihydrofuran and methyl acrylate[3] allowed the ^{13}C NMR chemical shifts (CDCl$_3$; δ from Me$_4$Si) and structures of **14** and **15** to be assigned.



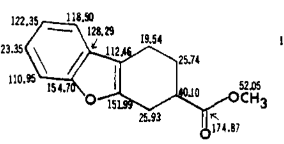
16



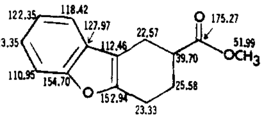
17



18



14



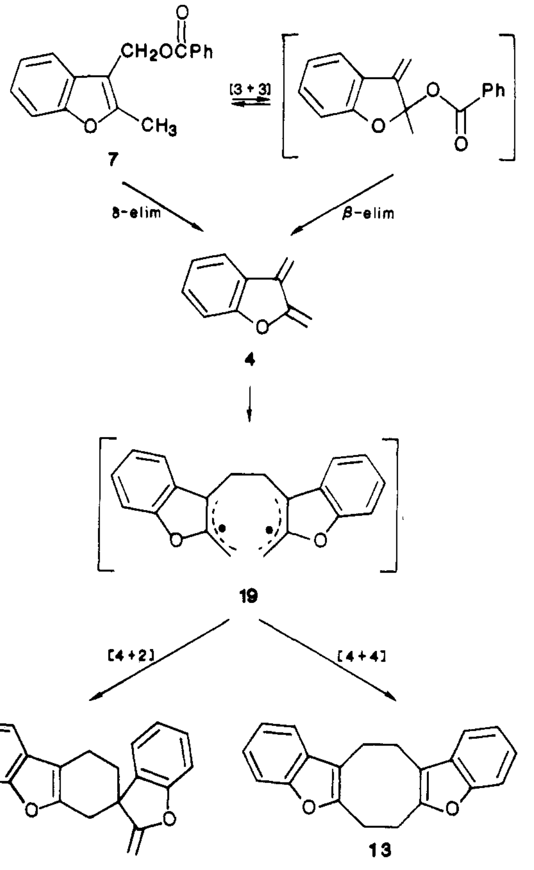
15

At least five of the signals of **14** were sufficiently separated from the corresponding signals of **15** that the areas of the peaks could be used to determine the isomer ratio.[25] An average of four determinations using this method indicated that the ratio of **14** to **15** was 3.0 to 1. This ratio is similar to that obtained for **17** and **18**.

Discussion

It has been proposed that the formation of 2,3-dimethylene-2,3-dihydrofuran (**1**) in the pyrolysis of (2-methyl-3-furyl)methyl benzoate (**2**) involves either a direct δ elimination of benzoic acid or proceeds by a two-step sequence involving a [3,3] shift of the benzoate group followed by β eliminatioin of benzoic acid.[3] The dimerization of **1**, which leads to a high yield of the head-to-head [4 + 4] dimer **3**, has been shown to proceed by a stepwise mechanism via a diradical intermediate.[4] This mechanism is strongly supported by the results of a secondary deuterium kinetic isotope effect study.[4]

Scheme II



7

4

19

12

13

The formation of 2,3-dimethylene-2,3-dihydrobenzofuran (**4**) in the FVP of (2-methyl-3-benzofuryl)methyl benzoate (**7**) can also be explained by either a direct δ elimination of benzoic acid or by a two-step sequence involving a [3,3] shift followed by β elimination of benzoic acid. Moreover, the dimerization of **4** can be explained by a diradical mechanism, but unlike **1**, **4** gives two dimers, the head-to-head [4 + 4] dimer **13**, and, as the major dimer, the [4 + 2] dimer **12**. There are four conceivable [4 + 2] dimers (each a racemate) and the only one observed is the one expected from the diradical (**19**) that leads to the [4 + 4] dimer **13**. Thus, we favor for the formation of both dimers stepwise mechanisms involving diradical **19**. However, a concerted mechanism for the formation of either dimer cannot be rigorously excluded. In Scheme II, our proposed pathways from **7** to **12** and **13** are presented.

A question that should be answered is why in the dimerization of the benzo analogue **4** is the major product a [4 + 2] dimer whereas in the dimerization of the parent furan *o*-quinodimethane, **1**, the major product is a [4 + 4] dimer? Possibly the ratio of [4 + 2] to [4 + 4] dimers is determined by the specific conformations of the diradical, which are determined by the orientation of the two monomers as they react to form the diradical. Presently we are studying substituted furan *o*-quinodimethanes in an

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[24] Platzer, N.; Basselier, J. J.; Demerseman, P. *Bull. Soc. Chim. Fr.* **1974**, *5*, 905.

[25] The ratio of **14** and **15** was determined by comparison of the five signals, δ 174.87, 40.10, 25.93, 25.74, 19.54, from **14** to the corresponding ones from **15**. It was assumed that the relaxation rates of the corresponding carbons in **14** and **15** are the same.

effort to answer this question.

Experimental Section

Methods and Materials. Some general methods have previously been described.[4] GLC analyses were performed using a Hewlett Packard HP 5840A instrument equipped with a 25-m, SP 2100 thin film (methyl silicone coated) capillary column. Elemental analyses were carried out by Spang Microanalytical Laboratory, Ann Arbor, Mi. Ethyl phenoxyacetate was purchased from Pfaltz and Bauer, Inc. Iodomethane-d_3 and methyl acrylate were purchased from Aldrich Chemical Company. Benzofuran-2,3-dicarboxylic acid (**11**) was prepared from ethyl phenoxyacetate by using the method reported previously.[21]

3-Benzofurancarboxylic Acid (8). A quantity of 1.00 g (4.9 mmol) of **11** was pyrolyzed at 700 °C and ca. 10^{-4} torr[22] in the usual manner.[4] The sample chamber was maintained at 100 °C during the entire pyrolysis. The brown solid which deposited in the pyrolysis tube outside the hot zone was washed out three times with 20-mL portions of anhydrous ether. The ether solutions were combined and extracted with 10% NaOH solution (5 × 20 mL). The aqueous solution was acidified with 10% HCl to give a yellow precipitate. The precipitate was filtered and washed successively with cold water (3 × 5 mL) and dried under reduced pressure to give 0.65 g (4.0 mmol, 81.6%) of **8**: mp 159–161 °C [lit.[26] mp 162 °C]; ^{1}H NMR (CDCl$_3$/acetone-d_6, 1:1) δ 8.40 (s, 1 H), 8.20–7.25 (m, 5 H); ^{13}C NMR (CDCl$_3$) δ 169.08, 155.81, 152.50, 125.57, 124.47, 122.13, 114.91, 114.06, 111.79; high resolution mass spectrum, calcd for $C_9H_6O_3$ 162.03170, measured 162.03152.

2-Methyl-3-benzofurancarboxylic Acid (9). To a solution of 1.00 g (6.17 mmol) of 3-benzofurancarboxylic acid (**8**) in 30 mL of tetrahydrofuran (dried over LiAlH$_4$) was added the lithiating agent (2.2 equiv of *n*-BuLi) dropwise at −78 °C with stirring under nitrogen. The reaction mixture was stirred at −78 °C for 30 min and 0 °C for another 30 min. A 1.30-g (9.25 mmol) quantity of iodomethane was added and the mixture was allowed to warm to room temperature and stirred overnight. The reaction mixture was poured into 75 mL of water and acidified with 1 M HCl. After separation the aqueous layer was extracted with ether (3 × 30 mL) and the organic layers were combined, dried (MgSO$_4$), and concentrated. The crude product was purified by recrystallization (from 1:1 ether and hexanes) to give 0.98 g (5.55 mmol; 90%) of **9**: mp 183–185 °C; IR (CS$_2$) 1680, 1285, 1240, 1175, 1104, 1085, 924 cm^{-1}; ^{1}H NMR (CDCl$_3$/acetone-d_6, 1:1) δ 8.20–7.20 (m, 5 H), 2.74 (s, 3 H); high resolution mass spectrum, calcd for $C_{10}H_8O_3$ 176.04735, measured 176.04662.

2-Methyl-3-benzofurfuryl Alcohol (10). To a stirred slurry of 0.26 g (6.82 mmol) of LiAlH$_4$ in 50 mL of anhydrous ether at 0 °C was added 1.20 g (6.82 mmol) of 2-methyl-3-benzofurancarboxylic acid (**9**) in 30 mL of anhydrous ether over a 5-min period. The resulting mixture was stirred at room temperature for 10 h. A standard workup procedure[27] gave 1.02 g (6.27 mmol; 92%) of **10**: mp 83–84 °C; IR (CS$_2$) 3600, 2940–2860, 1620, 1380, 1240, 1170, 1090, 990 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.60–7.05 (m, 4 H), 4.62 (s, 2 H), 2.37 (s, 3 H), 2.00 (br s, 1 H); high resolution mass spectrum, calcd for $C_{10}H_{10}O_2$ 162.06808, measured 162.06751.

(2-Methyl-3-benzofuryl)methyl Benzoate (7). A solution of 0.95 g (6.79 mmol) of benzoyl chloride in 20 mL of ether was added over a 10-min period to a stirred solution of 1.00 g (6.17 mmol) of 2-methyl-3-benzofurfuryl alcohol (**10**) and 0.94 g (9.26 mmol) of triethylamine in 50 mL of ether. The mixture was heated to reflux for 12 h, then 25 mL of water was added, and the mixture was stirred at room temperature for an additional 2-h period. The organic layer was separated, and the aqueous layer was extracted with ether (3 × 20 mL). The ether layers were combined and washed successively with 1 M HCl (3 × 10 mL), saturated NaHCO$_3$ (3 × 10 mL), and saturated NaCl (3 × 10 mL). After drying (MgSO$_4$) and removal of the solvent, the crude product was purified by column chromatography on silica gel (5% ether in hexanes) to give 1.49 g (5.61 mmol; 91%) of **7**: IR (thin film) 1725, 1460, 1270, 1180, 1110, 1095, 1070, 1030 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 8.40–7.40 (m, 9 H), 5.70 (s, 2 H), 2.65 (s, 3 H); high resolution mass spectrum calcd for $C_{17}H_{14}O_3$ 266.09430, measured 266.09518. Anal. Calcd: C, 76.66 H, 5.30. Found: C, 76.65; H, 5.24.

2-(Trideuteriomethyl)-3-benzofurancarboxylic Acid (9-d_3). A 1.00-g (6.17 mmol) quantity of 3-benzofurancarboxylic acid (**8**) was converted to **9**-d_3 by using 1.5 equiv of iodomethane-d_3 in the procedure described for the synthesis of **9**. Recrystallization of the crude product from 1:1 ether/hexanes yielded 1.02 g (5.68 mmol, 92%) of **9**-d_3: mp 184–185 °C; IR (CS$_2$) 1690, 1292, 1250, 1185, 1110, 1095 cm^{-1}; ^{1}H NMR (CDCl$_3$/acetone-d_6, 1:1) δ 8.45 (br s, 1 H), 8.20–7.20 (m, 4 H).

[2-(Trideuteriomethyl)-3-benzofuryl]methyl Benzoate (7-d_3). To a stirred slurry of 0.21 g (5.59 mmol) of LiAlH$_4$ in 50 mL of anhydrous ether at 0 °C was added 1.00 g (5.59 mmol) of 2-(trideuteriomethyl)-3-benzofurancarboxylic acid (**9**-d_3) in 30 mL of anhydrous ether over a 5-min period. The resulting mixture was stirred at room temperature for 10 h. A standard workup procedure[27] gave 0.88 g (5.31 mmol, 95%) of [2-(trideuteriomethyl)-3-benzofuryl]methyl alcohol (**10**-d_3): mp 83–84 °C; IR (CS$_2$) 3620, 2960–2880, 1620, 1385, 1245, 1175, 1125, 980 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.60–7.05 (m, 4 H), 4.63 (s, 2 H), 1.75 (br s, 1 H). Without further purification 0.80 g (4.85 mmol) of the alcohol was converted to **7**-d_3 by using the procedure described for the synthesis of **7**. The benzoate was purified by column chromatography silica gel (5% ether in hexanes) to give 1.16 g (4.31 mmol, 89%) of **7**-d_3: IR (thin film) 1715, 1450, 1260, 1245, 1095, 1060, 1020 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 8.40–7.40 (m, 9 H), 5.67 (s, 2 H); high resolution mass spectrum, calcd for $C_{17}H_{11}D_3O_3$ 269.11313, measured 269.11270.

General Pyrolysis Procedures. The furnace was maintained at temperatures ranging between 600 and 640 °C. A sample of the 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. 100 °C during the pyrolysis. A condenser inserted between the furnace and the liquid-nitrogen-cooled trap to collect the benzoic acid formed as a byproduct was cooled to ca. 0 °C. During the pyrolysis CS$_2$, and in some cases a reagent, was deposited into the trap through a side arm. Upon completion of the pyrolysis nitrogen was introduced into the system and the trap was warmed to −78 °C. CS$_2$ 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, filtered, and concentrated.

Pyrolysis of (2-Methyl-3-benzofuryl)methyl Benzoate (7). A 200-mg (0.752 mmol) quantity of **7** was pyrolyzed at 620 °C in the normal manner. The pyrolysate was collected in CS$_2$, dried (Na$_2$CO$_3$), and concentrated. GC and ^{1}H NMR analyses of the crude product mixture indicated that [4 + 2] dimer **12** and [4 + 4] dimer **13** were the two major products formed in a ratio of 4.1 to 1 in favor of **12**. Dimers **12** and **13** were separated by TLC using a preparative silica gel plate (5% ether in hexanes) and their ^{1}H NMR spectral data were recorded. **[4 + 2] dimer 12**: ^{1}H NMR (CDCl$_3$) see Figure 1; GC/MS (70 eV), *m/e* (relative intensity) 290.30 (0.78), 289.32 (9.52), 288.34 (41.03), 273.26 (10.45), 145.22 (11.54), 144.12 (100.00), 116.18 (8.72), 115.06 (52.42). **[4 + 4] dimer 13**: ^{1}H NMR (CDCl$_3$) δ 7.36–7.11 (m, 8 H), 3.33 (s, 4 H), 3.16 (s, 4 H); GC/MS (70 eV), *m/e* (relative intensity) 289.00 (6.29), 288.00 (22.38), 273.00 (3.50), 145.00 (11.19), 144.00 (100.00), 116.00 (9.79), 115.00 (51.75).

2,3-Dimethylene-2,3-dihydrobenzofuran (4). A 150-mg (0.564 mmol) quantity of (2-methyl-3-benzofuryl)methyl benzoate (**7**) was pyrolyzed at 610 °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 pyrolysis was completed, 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 ^{1}H NMR spectrum, after 500 scans, was recorded, indicating the presence of **4**: ^{1}H NMR (1:1 CS$_2$/CDCl$_3$, −60 °C) δ 7.43–6.90 (m, 4 H), 5.57 (s, 1 H), 5.54 (s, 1 H), 4.92 (d, J = 2.7 Hz, 1 H), 4.77 (d, J = 2.7 Hz, 1 H). Upon warming to room temperature, **4** dimerized forming **12** and **13**. Quantitative ^{1}H NMR analysis using a dibromoethane standard indicated that pyrolysis of **7** gave **4** in 35% yield and 85% of **4** was converted to **12** and **13** upon warming to room temperature.

Pyrolysis of [2-(Trideuteriomethyl)-3-benzofuryl]methyl Benzoate (7-d_3). A 220-mg (0.816 mmol) quantity of **7**-d_3 was pyrolyzed in the normal manner. The pyrolysate was collected

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in 4 mL of 1:1 $CS_2/CDCl_3$ and ^1H NMR spectral data were recorded at low temperature for **4**-d_2: ^1H NMR (1:1 $CS_2/CDCl_3$, −60 °C) δ 7.45–6.90 (m, 4 H), 5.58 (s, 1 H), 5.55 (s, 1 H). Upon warming to room temperature, 90% of **4**-d_2 was converted to **12**-d_4 and **13**-d_4 in a ratio of 4.4 to 1. After separation of **12**-d_4 and **13**-d_4 by TLC (silica gel plate, 5% ether in hexanes), their ^1H NMR spectral data were recorded. **12**-d_4: ^1H NMR ($CDCl_3$) δ 7.50–6.85 (m, 8 H), 2.94–2.80 (m, 2 H), 2.12–1.97 (m, 2 H). **13**-d_4: ^1H NMR ($CDCl_3$) δ 7.35–7.10 (m, 8 H), 3.15 (s, 4 H).

Diels–Alder Reaction of 4 with Methyl Acrylate. A 210-mg (0.789 mmol) quantity of (2-methyl-3-benzofuryl)methyl benzoate (**7**) was pyrolyzed at 630 °C. The pyrolysate was collected in 10 mL of a 1:1 mixture of methyl acrylate in CS_2 at −78 °C. The product was then slowly warmed to room temperature, dried (Na_2CO_3), and concentrated. TLC (silica gel plate, 5% ether in hexanes) yielded 64 mg (0.276 mmol, 35%) of 141.00 (12.14), 128.02 (10.57), 115.04 (29.67).

Diels–Alder Reactions of 4-d_2 with Methyl Acrylate. A 150-mg (0.557 mmol) quantity of [2-(trideuteriomethyl)-3-benzofuryl]methyl benzoate (**7**-d_3) was pyrolyzed at 630 °C. The pyrolysate was collected in 10 mL of 1:1 mixture of methyl acrylate in CS_2 at −78 °C. The product was then slowly warmed to room temperature, dried, and concentrated. TLC (silica gel plate, 5% ether in hexanes) yielded 51.7 mg (0.223 mmol, 40%) of the Diels–Alder adducts (**14**-d_2 and **15**-d_2): ^1H NMR ($CDCl_3$) δ 7.45–7.16 (m, 4 H), 3.75 (s, 3 H), 3.15–1.90 (m, 5 H); ^1H NMR (benzene-d_6) δ 7.42–7.12 (m, 4 H), 3.37 (s, 3 H), 3.33 (s, 3 H), 2.85–1.65 (m, 5 H).

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Registry No. **4**, 98115-18-5; **4**-d_2, 103981-45-9; **7**, 98115-19-6; **7**-d_3, 103981-42-6; **8**, 26537-68-8; **9**, 3265-74-5; **9**-d_3, 103981-40-4; **10**, 53839-34-2; **10**-d_3, 103981-41-5; **11**, 131-76-0; **12**, 103981-43-7; **12**-d_4, 103981-46-0; **13**, 103981-44-8; **13**-d_4, 103981-47-1; **14**, 103981-48-2; **14**-d_2, 103981-50-6; **15**, 103981-49-3; **15**-d_2, 103981-51-7; $H_2C{=}CHCO_2CH_3$, 96-33-3.

Alkylation and Oligomerization of the Lithium Enolate of 2-Norbornenones. Stereochemical Consequences of Enolate Aggregation

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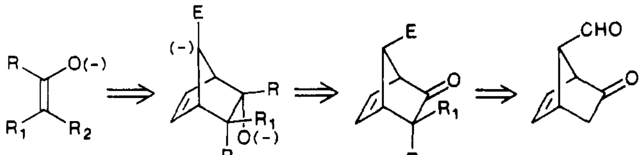
Alkylation of the lithium enolate of norbornenone in THF with alkyl halides gave a single trimeric oligomer containing one alkyl group as the major product. The structure of this diastereomer has been determined by ^1H and ^{13}C 2-D NMR techniques and analysis of relaxation times. Direct reaction in the aggregated enolate with the Zimmerman–House–Jackman cubic structure is implied. Compounds with a 7-anti substituent could be alkylated in satisfactory yield. The use of the dimethylhydrazone anion as an enolate equivalent gave good yields of 3-alkylnorbornenones (methyl, *n*-hexyl, benzyl). ^1H and ^{13}C NMR data for products and intermediates are reported.

Scheme I



The combination of the convenient industrial scale synthesis of 7-substituted norbornenones[1] with the anion-induced retro-Diels–Alder reaction[2] to generate specifically substituted enolates and olefins appeared attractive (Scheme I). In the course of this endeavor,[3] the alkylation of the lithium enolate of 2-norbornenone (II) was undertaken and a unique trimeric product (V) obtained under standard reaction conditions. A hypothesis is proposed for the preferential formation of trimer and the preference for only one of its 128 possible isomeric forms. Formation of V is postulated to occur through the Zimmerman–House–Jackman cubic structure for aggregated lithium enolates.[4] This contrasts with the enolate of 2-norbornanone which undergoes alkylation in good yield.[5] A practical alkylation of norbornenone is accomplished through the hydrazone methodology.[6] The synthetic results are presented first. The detailed nmr experiments necessary to establish the unique structure V is next. The discussion of how V is formed follows and then the Experimental Section. A compilation of ^{13}C shifts of substituted norbornanes is presented as supplementary material.

Results

Enolate Preparation and Alkylation. The lithium enolate of 2-norbornenone (II) was prepared by the addition of the ketone to lithium diisopropylamide (LDA) in THF. Quenching with propionaldehyde gave III as a single isomer in 84% isolated yield. This confirms that enolate II is stable and readily prepared in good yield.

Treatment of II with a series of alkyl halides gave poor yields of the anticipated 3-alkylnorbornenone (IV) (Table

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