dried, and stored as above. Acetonitrile (reagent grade, MCB) was distilled under vacuum from $CaH_2$, immediately prior to use. All spectra were recorded by using the X-band of an IBM ER-200D SRC spectrometer. Spectral simulations were done by using either the spectrometer's Aspect computer and the commercial IBM software package or an IBM PC using the simulation program developed by Stevenson and Reiter.[15]

**Ligand Syntheses.** Aza-15-crown-5 and aza-18-crown-6 were prepared as previously described.[9,11] 2-Nitrobenzyl chloride, 4-nitrobenzyl chloride, and *N*-bromosuccinimide were obtained from Aldrich Chemical Co. and were used without further purification. 2-Nitrotoluene (**3**) and 4-nitrotoluene were obtained from Aldrich and were distilled prior to use. Toluene-$d_8$ was obtained from MSD Isotopes and was used without further purification.

***N*-(2-Nitrobenzyl)aza-15-crown-5, 1.** Aza-15-crown-5 (3.03 g, 0.014 mol), $Na_2CO_3$ (2.91 g, 0.027 mol), MeCN (60 mL), and 2-nitrobenzyl chloride (2.70 g, 0.016 mol) were stirred at reflux for 24 h, cooled, filtered, and concentrated in vacuo. The residue was dissolved in $CHCl_3$ (50 mL) and extracted with 6 N HCl (2 × 50 mL). The combined aqueous phases were adjusted to pH 8-10 with $Na_2CO_3$ and extracted with $CHCl_3$ (2 × 100 mL). The organic phases were dried ($MgSO_4$) and concentrated in vacuo. Column chromatography (silica gel 60, $CHCl_3$) gave 4.78 g (96%) of **1** as a yellow oil with physical properties identical with those previously reported.[3b]

***N*-(2-Nitrobenzyl)aza-15-crown-5-$d_6$, 2.** 2-Nitrotoluene-$d_7$ was prepared from toluene-$d_8$ (10.0 g, 0.1 mol), $HNO_3$, HOAc, and $Ac_2O$ according to a literature procedure.[10] Kugelrohr distillation of the crude material (27-30 °C, 0.05 torr) gave a mixture of 2- and 4-nitrotoluene-$d_7$ (6.0 g, 42%). The mixture (2.0 g) was separated by column chromatography (120 g silica gel 60) to give 2-nitrotoluene-$d_7$, **4** (0.5 g, 3.6% total yield). The remaining material (1.5 g) was recovered after chromatography as a mixture of 2-nitrotoluene and 4-nitrotoluene.

The deuterated nitrotoluene mixture described above (2.88 g, 0.02 mol) was treated with *N*-bromosuccinimide (3.56 g, 0.02 mol) in $CCl_4$ according to a literature procedure.[16] A mixture of hexadeuterio-2- and hexadeuterio-4-nitrobenzyl bromides (2.21 g, 50%) was obtained by crystallization from hexanes.

The above described mixture of bromides (0.62 g, 0.028 mol) was treated with $Na_2CO_3$ (0.24 g, 0.046 mol) and aza-15-crown-5 (0.50 g, 0.023 mol) in MeCN (5 mL) at reflux for 24 h. The reaction mixture was cooled, filtered, and concentrated in vacuo. The mixture of 2- and 4-nitro lariat ethers was separated by chromatography (alumina, 2-PrOH/hexanes) to give **2** (36%) which was characterized as described for **1** above.

***N*-(4-Nitrobenzyl)aza-15-crown-15, 5,** was prepared from aza-15-crown-5 (3.03 g, 0.014 mol) and 4-nitrobenzyl chloride (2.39 g, 0.014 mol) as described for **1**. Column chromatography (silica gel 60, $CHCl_3$) gave 4.2 g (85%) of **5** as a yellow oil with physical properties identical with those reported.[3b]

***N*-(2-Nitrobenzyl)aza-18-crown-6, 6,** was prepared from aza-18-crown-6 (3.06 g, 0.012 mol) and 2-nitrobenzyl chloride as described for **1**. Column chromatography (silica gel 60, $CHCl_3$) gave **6** (3.9 g, 82%) as a yellow oil: $^1H$ NMR ($CDCl_3$, PPM) 2.73 (t, 4 H, $NCH_2$), 3.53 and 3.66 (t and m, 20 H, $OCH_2$), 3.98 (s, 2 H, benzyl), 7.3-7.9 (m, 4 H, Ar); IR (neat) 2840, 1520, 1440, 1350, 1300, 1240, 1110, 980, 940, 850, 780, 720 cm$^{-1}$. Anal. Calcd for $C_{19}H_{30}N_2O_7$: C, 57.26; H, 7.60; N, 7.03. Found: C, 56.96; H, 7.78; N, 7.00.

## Summary

Electrochemical reduction of nitroaromatic lariat ethers leads to strong intramolecular ion pairing between the macroring bound cation and the anionic sidearm. The strength and specificity of the interaction is related to the cation radius and the cavity size. This dependence is the result of increased coulombic interaction which confers added rigidity on the complex.

**Acknowledgment.** We thank the National Institutes of Health for grants which supported this work.

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[15] This program was kindly provided by G. R. Stevenson and R. Reiter, Department of Chemistry, Illinois State University, Normal, IL 61761.

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# The [4 + 4] Dimerization of 2,3-Dimethylene-2,3-dihydrofuran: Secondary Deuterium Kinetic Isotope Effect Evidence for a Two-Step Mechanism[1]

**Chin-Hsing Chou and Walter S. Trahanovsky***

*Contribution from Ames Laboratory and the Department of Chemistry, Iowa State University, Ames, Iowa 50011.* *Received November 20, 1985*

**Abstract:** 2,3-Dimethylene-2,3-dihydrofuran (**1a**), prepared by the flash vacuum pyrolysis of 2-methyl-3-furylmethyl benzoate (**2a**), rapidly dimerizes to form almost exclusively the [4 + 4] head-to-head dimer **3a**. Rate constants $k_a$, $k_b$, $k_c$, and $k_d$ were measured at several temperatures for the dimerization, a [4 + 4] cycloaddition, of **1a**, 2-methylene-3-dideuteriomethylene-2,3-dihydrofuran (**1b**), 2-dideuteriomethylene-3-methylene-2,3-dihydrofuran (**1c**), and 2,3-bis(dideuteriomethylene)-2,3-dihydrofuran (**1d**), respectively. At -30.0 °C these rate constants in L mol$^{-1}$ s$^{-1}$ were found to be $k_a = 6.223 \pm 0.458 \times 10^{-4}$, $k_b = 1.147 \pm 0.087 \times 10^{-3}$, $k_c = 6.750 \pm 0.602 \times 10^{-4}$, and $k_d = 1.169 \pm 0.086 \times 10^{-3}$, which indicates that $k_a \simeq k_c$ and $k_b/k_a \simeq k_d/k_a = 1.86$. It was found that the [4 + 4] dimerization rate of **1a** is virtually the same in solvents ranging from 5:1 to 1:5 $CS_2/CDCl_3$, a result not consistent with the involvement of a zwitterionic intermediate. The secondary deuterium kinetic isotope effect results and the insignificant solvent effects lead to the conclusion that the [4 + 4] dimerization of **1a** proceeds via a stepwise mechanism involving a diradical intermediate. The activation enthalpy, $\Delta H^{\ddagger}$, for the [4 + 4] dimerization of **1a** at 25 °C is 10.2 ± 0.3 kcal mol$^{-1}$ and the activation entropy, $\Delta S^{\ddagger}$, is -30.9 ± 1.2 entropy units.

Recently, we reported that 2,3-dimethylene-2,3-dihydrofuran (**1a**), generated by the flash vacuum pyrolysis (FVP) of 2-methyl-3-furylmethyl benzoate (**2a**), dimerizes quantitatively (>95%) to 4*H*,5*H*,9*H*,10*H*-cycloocta[1,2-*b*:6,5-*b*′]difuran (**3a**), the head-to-head, [4 + 4] dimer of **1a**.[2] As a rationalization of the formation of the high yield of **3a**, a stepwise mechanism involving diradical intermediate **4a** was proposed.[2] The dimerization of **1a** is an example of a facile, well-behaved thermal [4 + 4] cycloaddition. Cycloadditions can proceed in either a

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[1] (a) Presented in part at the 189th National Meeting of the American Chemical Society, Miami Beach, Florida, April-May 1985; paper ORGN 113. (b) Based on work by C. H. Chou in partial fulfillment of the requirements for the Ph.D. degree at Iowa State University.

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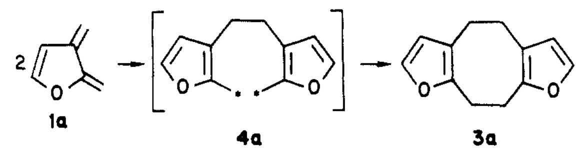
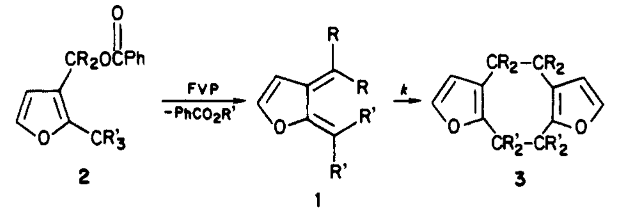


concerted or stepwise fashion,[3] and the mechanisms of many cycloadditions have been studied by a variety of experimental approaches.[4-6] In order to obtain experimental support for our proposed stepwise mechanism for the [4 + 4] cycloaddition of **1a**, we have carried out a secondary deuterium kinetic isotope effect (2° D KIE) study[7] of the cycloaddition. A series of deuterated 2,3-dimethylene-2,3-dihydrofurans, **1b–d**, were prepared by FVP of the corresponding deuterated 2-methyl-3-furylmethyl benzoates **2b–d**, and their rates of dimerization were measured and compared to that of **1a**. The results of this study are presented and discussed herein.



a, R=R'=H; b, R=D,R'=H; c, R=H, R'=D; d, R=R'=D

## Results

**Synthesis of 2-Methyl-3-furylmethyl Benzoates.** 2-Methyl-3-furylmethyl benzoate (**2a**) and 2-methyl-3-furylmethyl-$\alpha,\alpha$-$d_2$ benzoate (**2b**) were prepared from ethyl 2-methyl-3-furoate by using the method reported previously.[2] 2-Trideuteriomethyl-3-furylmethyl benzoate (**2c**) and 2-trideuteriomethyl-3-furylmethyl-$\alpha,\alpha$-$d_2$ benzoate (**2d**) were synthesized by starting from 3-furoic acid (**5**) as outlined in Scheme I. Acid **5** was converted to oxazoline **6** in order to take advantage of the ortho-directing ability of the oxazoline group[8,9] in the metalation reaction. The directing effect of the oxazoline group enabled the 2-trideuteriomethyl derivative **7** to be obtained uncontaminated by the 5-trideuteriomethyl isomer. Conversion of **7** to carboxylic acid **8** followed by reduction with either $LiAlH_4$ or $LiAlD_4$ and esterification gave ester **2c** or **2d**, respectively.

**Preparation of 2,3-Dimethylene-2,3-dihydrofurans.** 2,3-Dimethylene-2,3-dihydrofurans **1a–d** were prepared by the FVP of 2-methyl-3-furylmethyl benzoates **2a–d** at 670–680 °C and $10^{-4}$ torr. The yields of **1a–d** were in the range of 50–60%. The pyrolysis apparatus has been previously described[10] and is commercially available.[11] A condenser cooled to ca. −20 °C was inserted between the furnace and the liquid-nitrogen-cooled trap to collect unreacted starting material and the benzoic acid formed in the pyrolysis. This enabled us to obtain very pure monomer from the liquid-nitrogen-cooled trap.

**Determination of Rate Constants.** Rate constants for the [4 + 4] dimerization of 2,3-dimethylene-2,3-dihydrofurans **1a–d** were obtained by using a second-order rate expression.[12] In a typical kinetic run, the 2,3-dimethylene-2,3-dihydrofuran was prepared by pyrolyzing about 300 mg of the appropriate furfuryl benzoate. After the pyrolysis, the liquid-nitrogen-cooled trap was warmed to −78 °C and the walls of the trap were rinsed with 3 mL of degassed 1:1 $CS_2/CDCl_3$ at −78 °C. A weighed amount of the internal standard, dibromomethane, was added to the trap and some of the product solution was transferred to an NMR tube at −78 °C. The NMR tube was then transferred to a spectrometer with the temperature of the probe at the desired temperature. The temperature was kept constant and $^1H$ NMR spectra were recorded as a function of time. In Figure 1 are presented the $^1H$ NMR spectra for the dimerization of **1a** at −21.0 °C, a typical run. The concentrations of **1a** and **3a** were calculated by comparing their corresponding $^1H$ NMR peaks to that of the standard and these are listed in Table I. The last column in Table I is [**1a**] + 2[**3a**], the total concentration of **1a** and **3a** measured in terms of concentration of **1a**. The invariance of these numbers throughout the course of measurement indicates that the [4 + 4] dimerization of **1a** to **3a** is quantitative.

In Figure 2, a plot of $[\mathbf{1a}]^{-1}$ vs. time for the data in Table I is presented. The slope of the straight line, obtained from a least-squares fit, gives the value of $k_a$, $1.474 \pm 0.025 \times 10^{-3}$ L mol$^{-1}$ s$^{-1}$.

**Study of the 2° D KIE** on the [4 + 4] dimerization of **1a** was carried out by determining the rate constants, $k_a$, $k_b$, $k_c$, and $k_d$, for the [4 + 4] dimerization of **1a** and its deuterated derivatives **1b–d**.

**Scheme I**

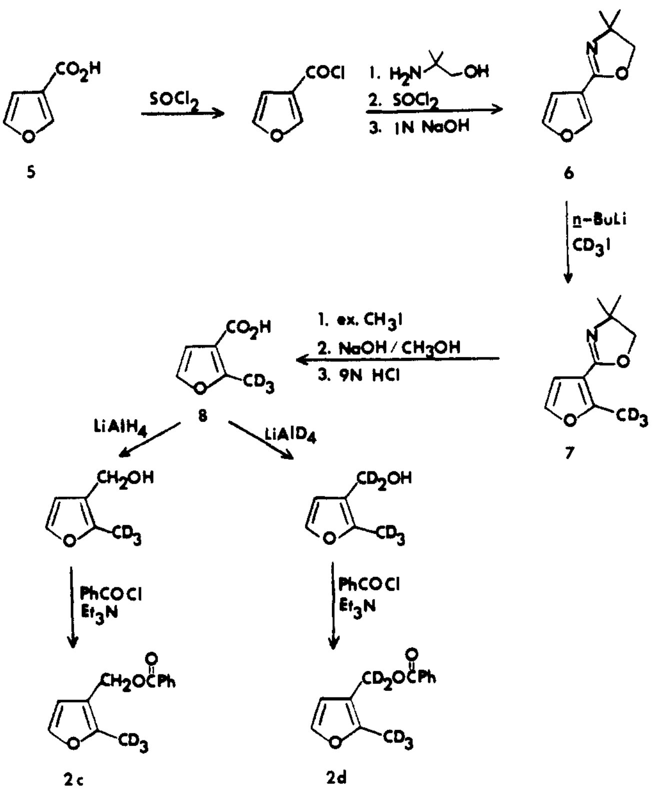


Table 1. A Typical Kinetic Run: Concentrations of 2,3-Dimethylene-2,3-dihydrofuran (**1a**) and Its [4 + 4] Dimer **3a** vs. Time at −21.0 °C in 1:1 $CS_2/CDCl_3$

| time, min | [**1a**], mol L$^{-1}$ | [**1a**]$^{-1}$, L mol$^{-1}$ | [**3a**], mol L$^{-1}$ | [**1a**] + 2[**3a**], mol L$^{-1}$ |
|---|---|---|---|---|
| 0.0 | 0.2859 | 3.497 | 0.01547 | 0.3168 |
| 8.0 | 0.2402 | 4.164 | 0.03862 | 0.3174 |
| 16.0 | 0.2012 | 4.970 | 0.05680 | 0.3148 |
| 24.0 | 0.1868 | 5.355 | 0.06631 | 0.3194 |
| 33.0 | 0.1584 | 6.314 | 0.08000 | 0.3184 |
| 42.0 | 0.1427 | 7.009 | 0.08720 | 0.3171 |
| 57.0 | 0.1191 | 8.396 | 0.09800 | 0.3151 |
| 73.0 | 0.1061 | 9.841 | 0.1062 | 0.3141 |
| 84.0 | 0.0909 | 11.000 | 0.1116 | 0.3142 |

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(12) (a) Espenson, J. H. *Chemical Kinetics and Reaction Mechanisms*; McGraw-Hillb New York, 1981. (b) Lowry, T. H.; Richardson, K. S. *Mechansim and Theory Organic Chemistry*; Harper & Row: New York, 1981, Chapter 2.

**Table II.** The Temperature Dependence of Rate Constant, $k_a$, for the [4 + 4] Dimerization of 2,3-Dimethylene-2,3-dihydrofuran (**1a**)

| temp, °C | temp, K | 1000/(*T* K) | $k_a$,[a] L mol$^{-1}$ s$^{-1}$ | log $k_a$ |
|---|---|---|---|---|
| −15.0 | 258.0 | 3.876 | 2.363 ± 0.036 × 10$^{-3}$ | −2.627 ± 0.007 |
| −21.0 | 252.0 | 3.968 | 1.474 ± 0.025 × 10$^{-3}$ | −2.832 ± 0.007 |
| −27.0 | 246.0 | 4.065 | 7.473 ± 0.137 × 10$^{-4}$ | −3.127 ± 0.008 |
| −33.0 | 240.0 | 4.167 | 4.631 ± 0.121 × 10$^{-4}$ | −3.334 ± 0.011 |
| −39.0 | 234.0 | 4.274 | 2.393 ± 0.059 × 10$^{-4}$ | −3.621 ± 0.011 |
| −46.0 | 227.0 | 4.405 | 1.355 ± 0.031 × 10$^{-4}$ | −3.868 ± 0.010 |
| −50.0 | 223.0 | 4.484 | 8.855 ± 0.381 × 10$^{-5}$ | −4.053 ± 0.019 |

[a] Rate constants were measured in 1:1 $CS_2/CDCl_3$.

**Table III.** Rate Constants for the [4 + 4] Dimerization of 2,3-Dimethylene-2,3-dihydrofuran (**1a**) and Its Deuterated Derivatives **1b–d**

| temp, °C | $k_a$,[a] L mol$^{-1}$ s$^{-1}$ | $k_b$,[b] L mol$^{-1}$ s$^{-1}$ | $k_c$,[c] L mol$^{-1}$ s$^{-1}$ | $k_d$,[d] L mol$^{-1}$ s$^{-1}$ |
|---|---|---|---|---|
| −15.0 | 2.270 ± 0.167 × 10$^{-3}$ | 4.093 ± 0.311 × 10$^{-3}$ | 2.473 ± 0.221 × 10$^{-3}$ | 4.174 ± 0.308 × 10$^{-3}$ |
| −30.0 | 6.223 ± 0.458 × 10$^{-4}$ | 1.147 ± 0.087 × 10$^{-3}$ | 6.750 ± 0.602 × 10$^{-4}$ | 1.169 ± 0.086 × 10$^{-3}$ |
| −45.0 | 1.435 ± 0.106 × 10$^{-4}$ | 2.712 ± 0.206 × 10$^{-4}$ | 1.548 ± 0.138 × 10$^{-4}$ | 2.763 ± 0.204 × 10$^{-4}$ |

[a] Data were obtained by graphic interpolation of a plot of log $k_a$ vs. 1000/*T* which is shown in Figure 3. [b] Data were obtained by graphic interpolation of a plot of log $k_b$ vs. 1000/*T*. [c] Data were obtained by graphic interpolation of a plot of log $k_c$ vs. 1000/*T*. [d] Data were obtained by graphic interpolation of a plot of log $k_d$ vs. 1000/*T*.

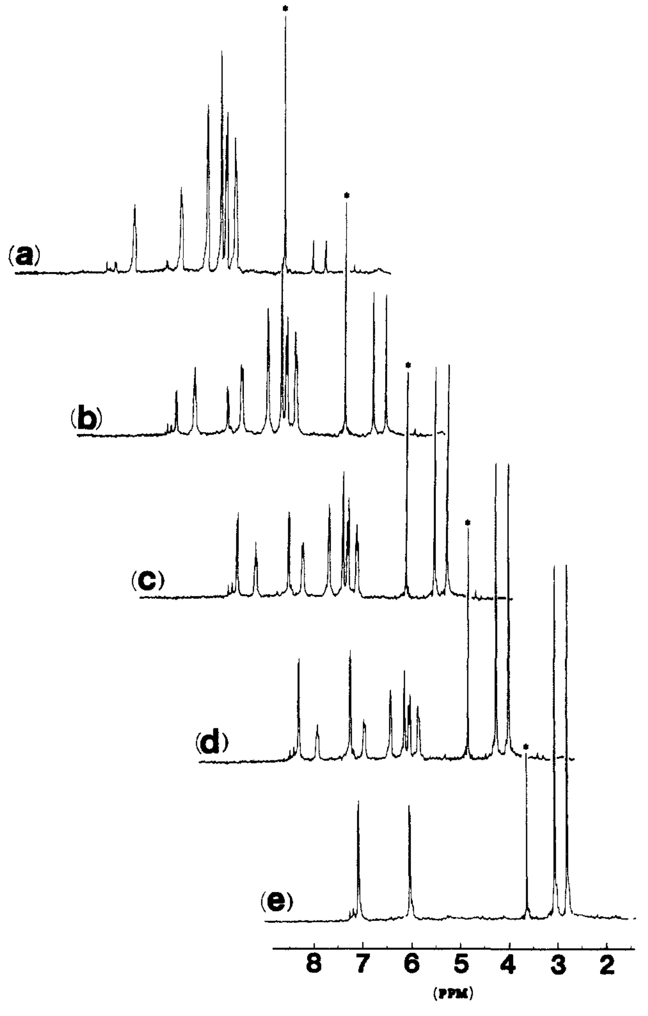


**Figure 1.** $^1$H NMR spectra of 2,3-dimethylene-2,3-dihydrofuran (**1a**) recorded vs. time at −21.0 °C in 1:1 $CS_2/CDCl_3$ (* = internal standard, $BrCH_2CH_2Br$): (a) time = 0.0 min; (b) time = 8.0 min; (c) time = 24.0 min; (d) time = 42.0 min; (e) time = 24 h at 35 °C.

**Table IV.** Secondary Deuterium Kinetic Isotope Effects Observed for the [4 + 4] Dimerization of 2-Methylene-3-dideuteriomethylene-2,3-dihydrofuran (**1b**) and 2-Dideuteriomethylene-3-methylene-2,3-dihydrofuran (**1c**)

| temp, °C | 2° D KIE per deuterium, $k_D/k_H$,[a] for reaction **21b** → **3b** | 2° D KIE per deuterium, $k_D/k_H$,[b] for reaction **21c** → **3c** |
|---|---|---|
| −15.0 | 1.16 ± 0.03 | 1.02 ± 0.03 |
| −30.0 | 1.17 ± 0.03 | 1.02 ± 0.03 |
| −45.0 | 1.17 ± 0.03 | 1.02 ± 0.03 |
| | av 1.17 ± 0.03 | av 1.02 ± 0.03 |

[a] $k_D/k_H = (k_b/k_a)^{1/4}$. [b] $k_D/k_H = (k_c/k_a)^{1/4}$.

**Table V.** Rate Constants for the [4 + 4] Dimerization of 2,3-Dimethylene-2,3-dihydrofuran [**1a**) at −30.0 °C in Mixtures of $CS_2/CDCl_3$

| ratio of $CS_2$ to $CDCl_3$ | $k_a$, L mol$^{-1}$ s$^{-1}$, at −30.0 °C |
|---|---|
| 5:1 | 6.406 ± 0.188 × 10$^{-4}$ [a] |
| 2:1 | 5.701 ± 0.172 × 10$^{-4}$ [a] |
| 1:1 | 6.223 ± 0.458 × 10$^{-4}$ [b] |
| 1:2 | 5.778 ± 0.128 × 10$^{-4}$ [a] |
| 1:5 | 5.720 ± 0.159 × 10$^{-4}$ [a] |

[a] Rate constants, $k_a$'s, were obtained from an average of two kinetic runs. [b] Data were obtained by graphical interpolation of a plot of log $k_a$ vs. 1000/*T* which is shown in Figure 3.

The rate constants for the [4 + 4] dimerization of **1a**, $k_a$, determined at various temperatures are listed in Table II. Also included in Table II are the reciprocal of temperatures, 1000/(*T* K), and the logarithm of $k_a$, log $k_a$. In Figure 3, a plot of log $k_a$ vs. 1000/*T*, an Arrhenius equation plot of the data in Table II,[12] is presented. The slope of the straight line, obtained from a least-squares fit, gives the value of $-10^{-3}E_a/2.303R = -2.351 \pm 0.058$ K, and the intercept of the line gives log $A = 6.467 \pm 0.243$. Hence, the activation energy, $E_a$, of the [4 + 4] dimerization of 2,3-dimethylene-2,3-dihydrofuran (**1a**) is 10.75 ± 0.27 kcal mol$^{-1}$, and the preexponential factor, *A*, is 2.93 ± 1.28 × 10$^6$ L mol$^{-1}$ s$^{-1}$.

In Figures 4–6 the $^1$H NMR spectra for kinetic runs of **1b** (at −30.0 °C), **1c** (at −26.0 °C), and **1d** (at −30.0 °C), respectively, are presented. Plots for these data were also very good, comparable to those obtained for **1a**.

As a summary of the 2° D KIE study, the rate constants for the [4 + 4] dimerization of 2,3-dimethylene-2,3-dihydrofuran (**1a**) and its deuterated derivatives **1b–d** at −15.0, −30.0, and −45.0 °C are listed in Table III. Data were obtained by graphical interpolation of the plots of log *k* vs. 1000/*T*. Clearly, the [4 + 4] dimerizations of **1b** and **1d** both showed 2° D KIE's and, within experimental error, to the same extent, while no 2° D KIE was observed for the dimerization of **1c**. In Table IV, the 2° D KIE's per deuterium calculated for the [4 + 4] dimerization of **1b** and **1c** are listed. The average 2° D KIE per deuterium obtained for the [4 + 4] dimerization of **1b**, $k_D/k_H = (k_b/k_a)^{1/4}$, is 1.17 ± 0.03 and that for the [4 + 4] dimerization of **1c**, $k_D/k_H = (k_c/k_a)^{1/4}$, is 1.02 ± 0.03.

**Study of the solvent effects on the reaction rate** was carried out by measuring the dimerization rate of **1a** in mixtures of carbon disulfide ($CS_2$) and chloroform-$d_1$ ($CDCl_3$). In Table V, the rate constants for the [4 + 4] dimerization of **1a** determined at −30.0

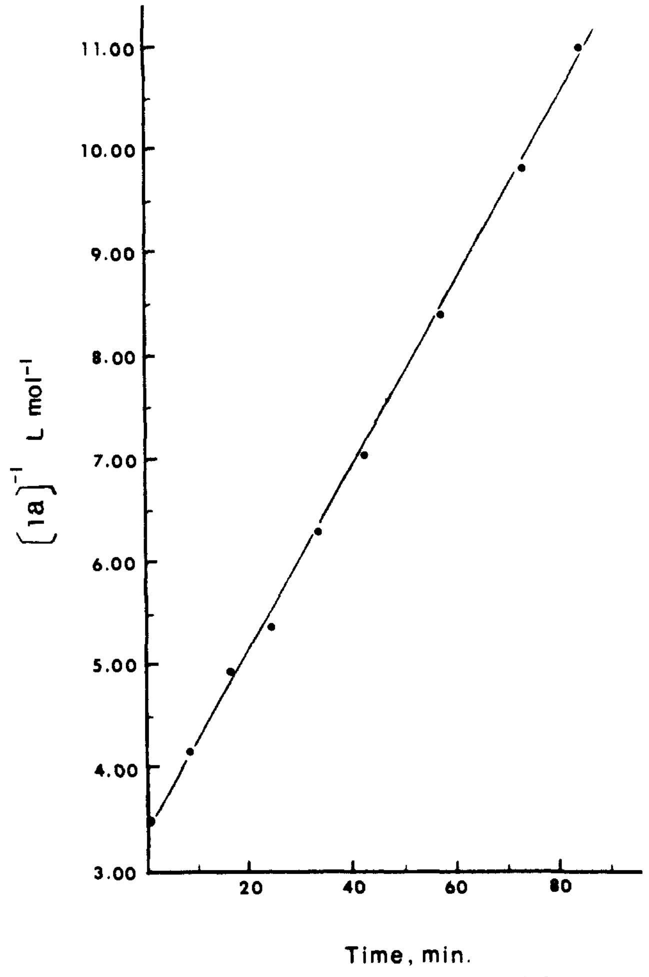


**Figure 2.** Plot of reciprocal of concentration of 2,3-dimethylene-2,3-dihydrofuran (**1a**), [**1a**]$^{-1}$, vs. time at −21.0 °C in 1:1 $CS_2/CDCl_3$. Data were obtained from Table I. The slope of the straight line = $k_a$ = 1.474 ± 0.025 × $10^{-3}$ L mol$^{-1}$ s$^{-1}$.

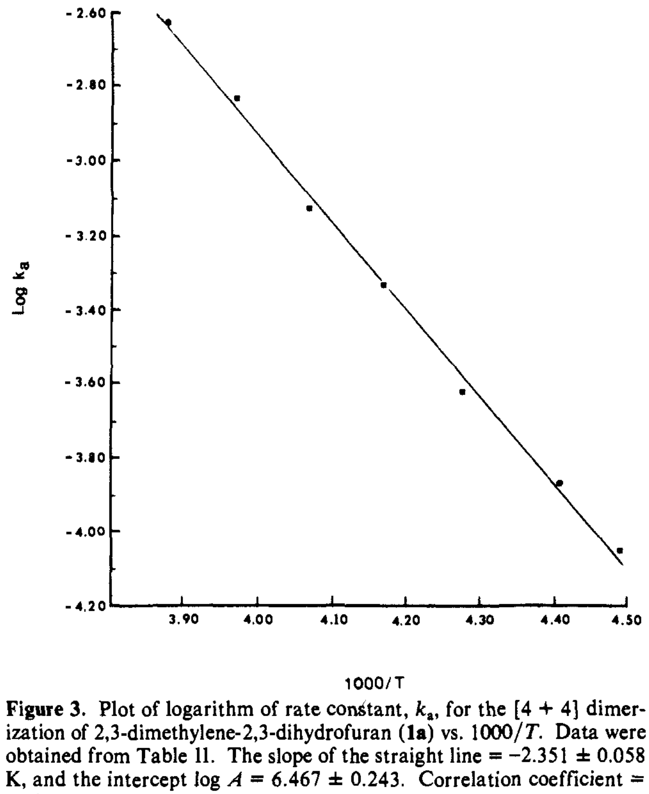


**Figure 3.** Plot of logarithm of rate constant, $k_a$, for the [4 + 4] dimerization of 2,3-dimethylene-2,3-dihydrofuran (**1a**) vs. 1000/$T$. Data were obtained from Table II. The slope of the straight line = −2.351 ± 0.058 K, and the intercept log $A$ = 6.467 ± 0.243. Correlation coefficient = −0.9985.

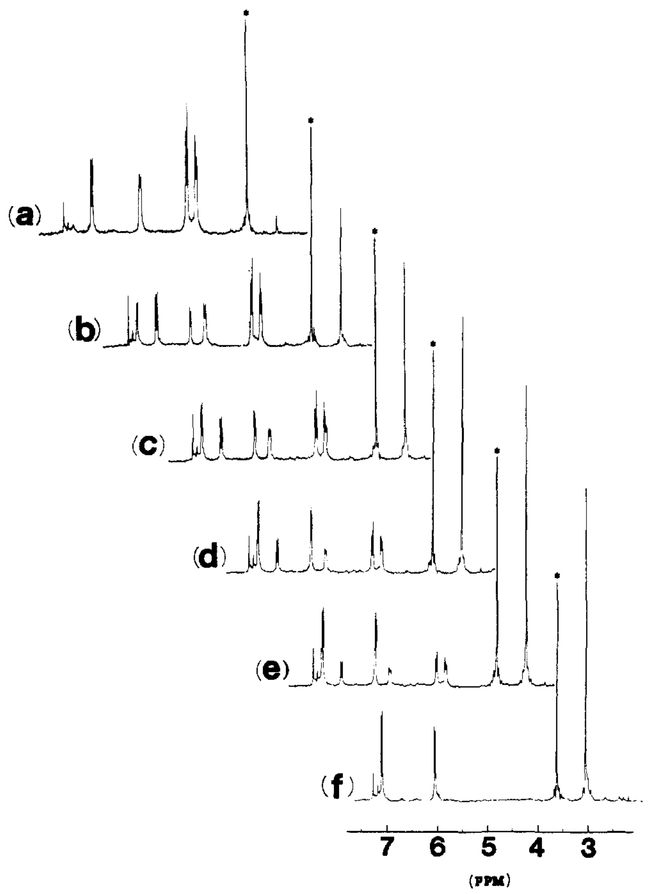


**Figure 4.** $^1H$ NMR spectra of 2-methylene-3-dideuteriomethylene-2,3-dihydrofuran (**1b**) recorded vs. time at −30.0 °C in 1:1 $CS_2/CDCl_3$ (* = internal standard, $BrCH_2CH_2Br$): (a) time = 0.0 min; (b) time = 28.0 min; (c) time = 53.0 min; (d) time = 88.0 min; (e) time = 138.0 min; (f) time = 24 h at 35 °C.

**Table VI.** Activation Parameters for the [4 + 4] Dimerization of 2,3-Dimethylene-2,3-dihydrofuran (**1a**) and Its Derivatives **1b–d**

| reaction | $E_a$, kcal mol$^{-1}$ | log $A$ | $\Delta H^{\ddagger}$, at 25 °C, kcal mol$^{-1}$ | $\Delta S^{\ddagger}$, at 25 °C, cal K$^{-1}$ mol$^{-1}$ |
|---|---|---|---|---|
| 2**1a** → **3a** | 10.8 ± 0.3 | 6.47 ± 0.24 | 10.2 ± 0.3 | −30.9 ± 1.2 |
| 2**1b** → **3b** | 10.6 ± 0.3 | 6.57 ± 0.24 | 9.98 ± 0.26 | −30.4 ± 1.1 |
| 2**1c** → **3c** | 10.8 ± 0.3 | 6.54 ± 0.26 | 10.2 ± 0.3 | −30.6 ± 1.2 |
| 2**1d** → **3d** | 10.6 ± 0.3 | 6.58 ± 0.26 | 9.98 ± 0.28 | −30.4 ± 1.2 |

°C in mixtures of 5:1, 2:1, 1:1, 1:2, and 1:5 $CS_2/CDCl_3$ are presented. It was found that in these solvent mixtures there is no significant difference in the reaction rate.

**Activation Parameters.** According to the Arrhenius equation, the temperature dependence of the rate constants discloses the values of the activation energy, $E_a$, and the preexponential factor, $A$.[12] Analogous quantities, the activation enthalpy, $\Delta H^{\ddagger}$, and the activation entropy, $\Delta S^{\ddagger}$, can be obtained from the Eyring equation.[12]

In Table VI, the activation parameters, $E_a$, log $A$, $\Delta H^{\ddagger}$ (at 25 °C), and $\Delta S^{\ddagger}$ (at 25 °C), calculated for the [4 + 4] dimerizations of **1a** and its derivatives **1b–d** are listed. The activation enthalpies, $\Delta H^{\ddagger}$'s, for all the reactions studied are in the vicinity of 10 kcal mol$^{-1}$ and the activation entropies, $\Delta S^{\ddagger}$'s, are about −30 entropy units.

## Discussion

The 2° D KIE, a change of rate that results from substitution of hydrogen with deuterium at a bond not being broken in the reaction, is a widely used tool for elucidating reaction mechanism.[7] The 2° D KIE's at carbon undergoing a change in hybridization are well established as being normal, i.e., $k_H/k_D > 1$, for the direction $sp^3 \rightarrow sp^2$ and inverse, $k_D/k_H > 1$, for a change in the

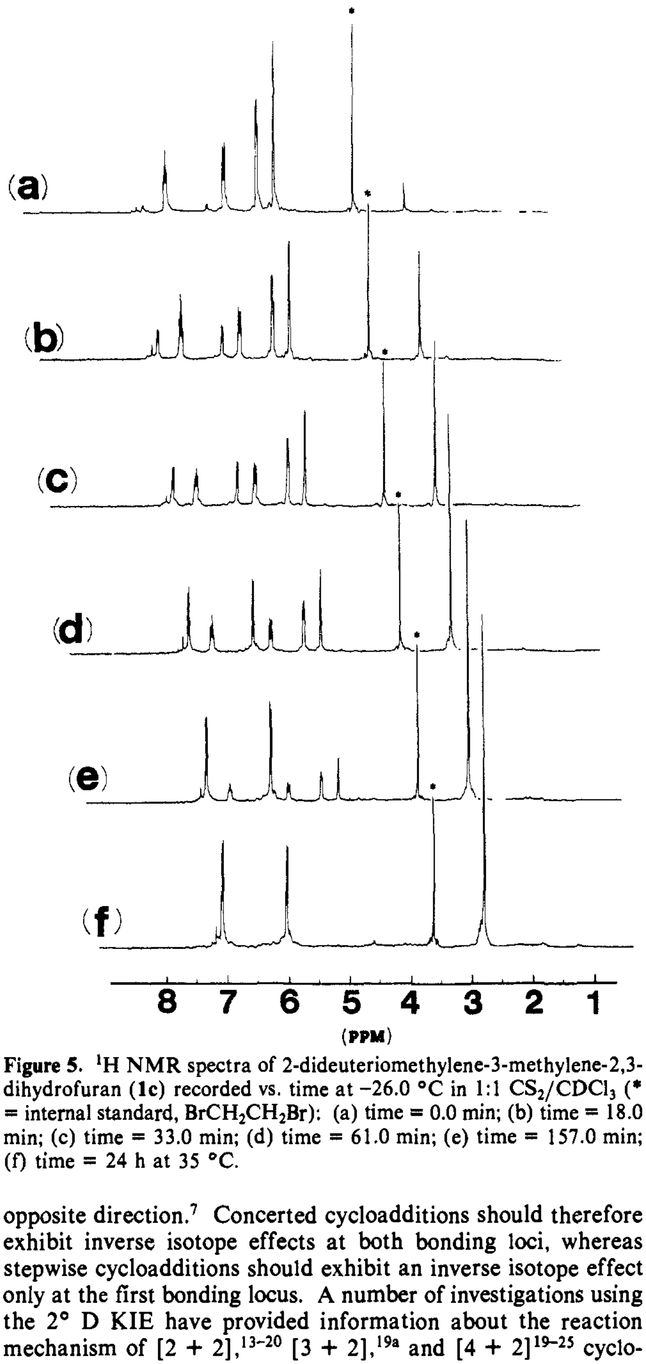


**Figure 5.** $^1$H NMR spectra of 2-dideuteriomethylene-3-methylene-2,3-dihydrofuran (**1c**) recorded vs. time at −26.0 °C in 1:1 $CS_2/CDCl_3$ (* = internal standard, $BrCH_2CH_2Br$): (a) time = 0.0 min; (b) time = 18.0 min; (c) time = 33.0 min; (d) time = 61.0 min; (e) time = 157.0 min; (f) time = 24 h at 35 °C.

opposite direction.[7] Concerted cycloadditions should therefore exhibit inverse isotope effects at both bonding loci, whereas stepwise cycloadditions should exhibit an inverse isotope effect only at the first bonding locus. A number of investigations using the 2° D KIE have provided information about the reaction mechanism of [2 + 2],[13-20] [3 + 2],[19a] and [4 + 2][19-25] cycloadditions.

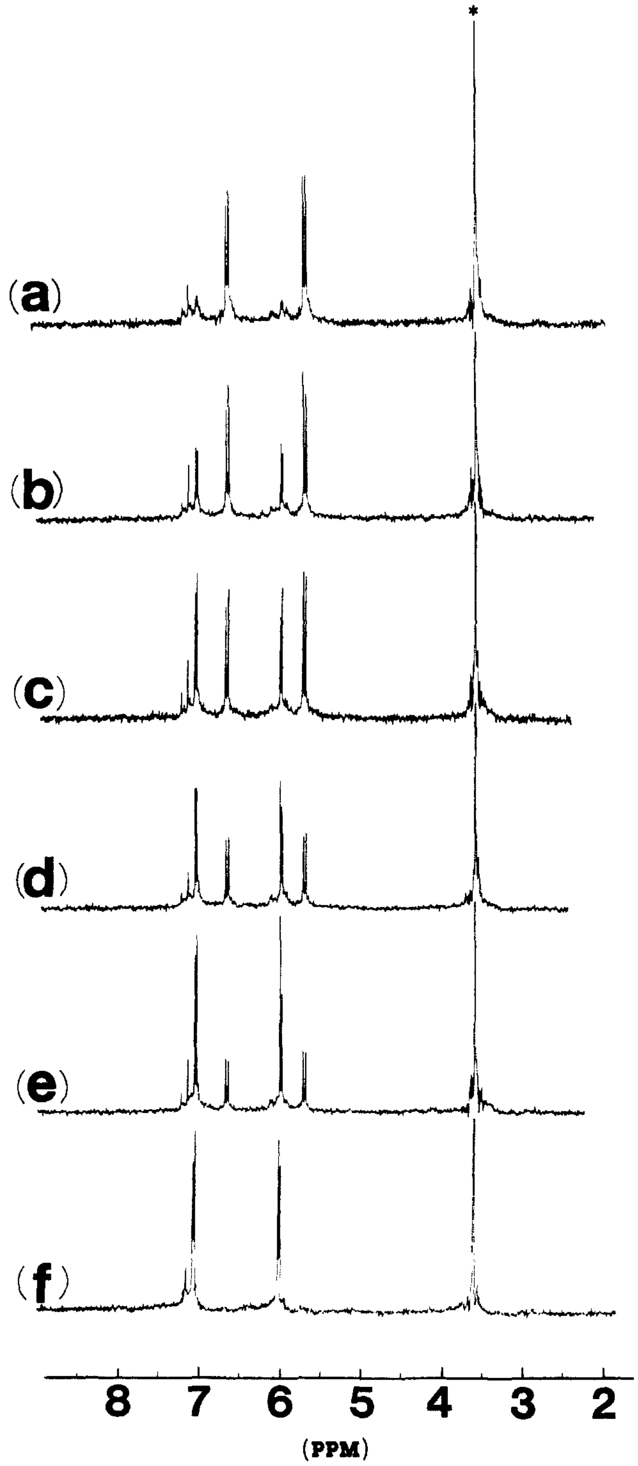
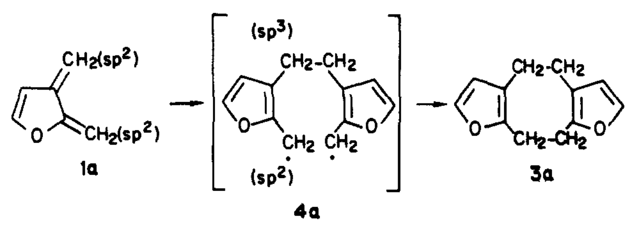


**Figure 6.** $^1$H NMR spectra of 2,3-bis(dideuteriomethylene)-2,3-dihydrofuran (**1d**) recorded vs. time at −30.0 °C in 1:1 $CS_2/CDCl_3$ (* = internal standard, $BrCH_2CH_2Br$): (a) time = 0.0 min; (b) time = 10.0 min; (c) time = 20.0 min; (d) time = 40.0 min; (e) time = 68.0 min; (f) time = 24 h at 35 °C.

Our study of the rates of dimerization of the undeuterated and deuterated 2,3-dimethylene-2,3-dihydrofurans **1a–d** reveals that $k_a \cong k_c$ and $k_b/k_a \cong k_d/k_a \cong 1.8$. This indicates that in the rate-determining step there is bonding at the 3-methylene position but not at the 2-methylene position, a result which firmly supports the stepwise mechanism involving diradical **4a**.



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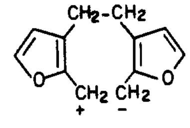
These results are also consistent with a stepwise mechanism involving zwitterionic intermediate **9**. However, experimental results which do not support the involvement of zwitterionic intermediate **9** were obtained from the study of solvent effects. It was found that the [4 + 4] dimerization rate of **1a** is virtually the same in solvents ranging from 5:1 to 1:5 of $CS_2/CDCl_3$.

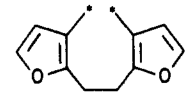


**9**

It is known that stepwise cycloadditions involving zwitterionic intermediates are strongly accelerated by polar solvents.[5,6] Huisgen and co-workers[26,27] have studied the solvent effects on the reactions of tetracyanoethylene (TCNE) with olefins, a type of [2 + 2] cycloaddition that is known to involve zwitterionic intermediates, and have reported that the dependence of TCNE cycloaddition constants on solvent polarity is great: $k_{\text{acetonitrile}}/k_{\text{cyclohexane}}$ amounts to 29000 for *p*-propenylanisole (**10**) and 10800 for ethyl isobutenyl ether (**11**). Also, $k_{\text{acetonitrile}}/k_{CCl_4}$ is 17000 for 2,3-dihydrofuran-4*H*-pyran (**12**). The log *k* values for these three [2 + 2] cycloadditions, measured in ten solvents, correlate linearly with $E_T$ values of Reichardt,[28] an empirical parameter of solvent polarity based on the solvatochromism of a pyridinium phenoxide. The rates of all three [2 + 2] cycloadditions, i.e, TCNE with **10**, **11**, and **12**, are found to be about 100 times faster in $CHCl_3$ ($E_T$ = 39.1) than in $CCl_4$ ($E_T$ = 32.5). The same magnitude of solvent effect would be expected between $CHCl_3$ and $CS_2$ ($E_T$ = 32.6), since the latter has the same solvent polarity as that of $CCl_4$. On the basis of the above consideration, if zwitterionic intermediate **9** were indeed involved in the [4 + 4] dimerization of **1a**, one would expect at least some degree of solvent effect in going from a ratio of 5:1 to 1:5 $CS_2/CDCl_3$. The virtually constant reaction rates that have been observed support the diradical intermediate.

Thus, we conclude on the basis of the 2° D KIE and solvent effect studies that the [4 + 4] cycloaddition of **1a** proceeds in a stepwise fashion involving diradical intermediate **4a** as the precursor of the [4 + 4] dimer **3a**. Although a number of studies of the mechanism of cycloadditions have made use of the 2° D KIE,[13-25] our study is one of the few that involved measurement of the absolute (not the relative) rate constants of the cycloaddition (not the retrocycloaddition). Moreover, compared to the other studies, our rate differences are quite large and definitive since our reaction is a very well-behaved one and involves four hydrogens or deuteriums at each bonding site.

It is worth noting that the intermediacy of diradical **4a**, rather than diradical **13**, in the [4 + 4] cycloaddition of **1a** is consistent with greater stability of **4a** and this is in good agreement with



**13**

the results of Strom, Russell, and Schoeb which show that hydrogen atom abstraction by the phenyl radical is faster for 2-methylfuran than for 3-methylfuran.[29]

Finally, although low activation enthalpies ($\Delta H^{*} < 25$ kcal mol$^{-1}$) and highly negative activation entropies ($\Delta S^{*}$ in the range of −40 to −30 entropy units) are generally expected for concerted cycloaddition reaction,[5,6] they are not sufficient to be the basis for differentiating concerted from stepwise cycloadditions. The values of the activation parameters obtained for the [4 + 4] cycloaddition of **1a**, $\Delta H^{*} \simeq 10$ kcal mol$^{-1}$ and $\Delta S^{*} \simeq -30$ entropy units, which lie in the same range are consistent with a facile bimolecular step leading to the diradical intermediate.

The initial conformation of the diradical intermediate **4a** and the conformations involved in going from the initial conformation to the dimer are details of the mechanism which are still unclear. Studies are in progress in our laboratories which should provide information about these conformations.

## Experimental Section

**Methods and Materials.** Some general methods have been described previously.[30] $^1$H NMR spectra were recorded on Varian A-60, JOEL FX-90Q, or NICOLET-300 spectrometers. $^{13}$C NMR spectra were recorded on JOEL FX-90Q or NICOLET-300 spectrometers. Infrared spectra were measured on Beckman-IR-4250 or Beckman Acculab 2 spectrometers. High-resolution mass spectra were measured with an Associated Electronics Industries MS-902 instrument at 70 eV. Gas chromatography/mass spectral analyses (GC/MS) were performed with use of a Finnigan 4000 instrument and an INCOS data system. 3-Furoic acid, 2-amino-2-methyl-1-propanol, and iodomethane-$d_3$ were purchased from Aldrich Chemical Co. 2-Methyl-3-furylmethyl benzoate (**2a**) and 2-methyl-3-furyl-methyl-$\alpha,\alpha$-$d_2$ benzoate (**2b**) were prepared from ethyl 2-methyl-3-furoate[31] by using the method reported previously.[2]

**2-(3-Furyl)-4,4-dimethyl-2-oxazoline (6).** A 15.0-g (0.134 mol) quantity of 3-furoic acid was added to 50.0 g (0.402 mol) of thionyl chloride, and the mixture was stirred at room temperature for 24 h. The excess thionyl chloride was removed by simple distillation, and the remaining dark oil was distilled under reduced pressure to yield 14.2 g (0.109 mol; 81.3%) of 3-furoyl chloride: bp 52–53 °C (16 mmHg) [lit.[32] bp 78–80 °C (55 mmHg)]; $^1$H NMR ($CDCl_3$) δ 8.30 (br s, 1 H), 7.60 (br s, 1 H), 6.86 (b s, 1 H). To a stirred solution of 14.2 g (0.109 mol) of 3-furoyl chloride in 50 mL of methylene chloride a solution of 2-amino-2-methyl-1-propanol (20.0 g, 0.22 mol) in 100 mL of methylene chloride was added dropwise while maintaining the temperature below 20 °C. The mixture was stirred at room temperature for 3 h and washed with water, and the organic layer was dried ($MgSO_4$). After removal of the solvent, the residue was suspended in 100 mL of benzene and a 38.9-g (0.327 mol) quantity of thionyl chloride was added dropwise with stirring while maintaining the temperature below 30 °C. After the mixture was stirred at room temperature for 10 h, the benzene was removed at aspirator pressure, the residue was dissolved in 100 mL of water, and the solution was basified with 1 N aqueous NaOH and extracted with ether (2 × 100 mL). After drying ($MgSO_4$) and removal of the solvent, the crude product was purified by column chromatography on silica gel (50% ether in hexanes) to yield 13.9 g (83.9 mmol; 77%) of **6**: mp 64 °C; IR ($CS_2$) 1678, 1324, 1165, 1110, 1013, 998, 984 cm$^{-1}$; $^1$H NMR ($CDCl_3$) δ 7.90 (br s, 1 H), 7.45 (br s, 1 H), 6.80 (br s, 1 H), 4.04 (s, 2 H), 1.37 (s, 6 H); high-resolution mass spectrum, calculated for $C_9H_{11}O_2N$ 165.07898, measured 165.07854.

**2-(2-Trideuteriomethyl-3-furyl)-4,4-dimethyl-2-oxazoline (7).** To a solution of 4.52 g (27.4 mmol) of 2-(3-furyl)-4,4-dimethyl-2-oxazoline (**6**) in 100 mL of dry ether ($LiAlH_4$) 1.1 equiv of *n*-butyllithium in hexanes was added dropwise at −78 °C with stirring under nitrogen. The reaction mixture was stirred at −78 °C for 15 min and at 0 °C for another 30 min, a 5.95-g (41.1 mmol) quantity of iodomethane-$d_3$ was added, and the mixture was allowed to warm up to room temperature and stirred for 3 h. The mixture was then poured into 100 mL of water. After separation, the aqueous layer was extracted with ether (2 × 30 mL) and the combined organic layers were dried ($MgSO_4$) and evaporated. The crude product was purified by column chromatography on silica gel (50% ether in hexanes) to give 4.64 g (25.5 mmol; 93%) of **7**: IR (thin film) 1670, 1615, 1437, 1315, 1240, 1146, 1063, 1005 cm$^{-1}$; $^1$H NMR ($CDCl_3$) δ 7.26 (d, *J* = 2.0 Hz, 1 H), 6.66 (d, *J* = 2.0 Hz, 1 H), 4.03 (s, 2 H), 2.35 (s, 6 H); high-resolution mass spectrum, calculated for $C_{10}H_{10}D_3O_2N$ 182.11346, measured 182.11380.

**2-Trideuteriomethyl-3-furoic Acid (8).** A 11.3-g (62.1 mmol) quantity of **7** was converted to **8** by the alkaline hydrolysis procedure of Meyers and co-workers[33] with the modification that **7** was stirred in the presence of an excess of iodomethane for 1 week instead of overnight. The crude product was prufied by recrystallization from hexanes to give 7.50 g (58.1 mmol; 93.6%) of **8**: mp 97–98 °C; IR ($CS_2$) 3200–2400, 1685, 1305, 1242, 1204, 1176, 1137, 1075 cm$^{-1}$; $^1$H NMR ($CDCl_3$) δ 9.58 (br, 1 H), 7.24 (d, *J* = 2.0 Hz, 1 H), 6.66 (d, *J* = 2.0 Hz, 1 H); high-resolution

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mass spectrum, calculated for $C_6H_3D_3O_3$ 129.05053, measured 129.05067.

**2-Trideuteriomethyl-3-furylmethyl Benzoate (2c).** To a stirred slurry of 0.956 g (25.2 mmol) of lithium aluminum hydride in 20 mL of dry ether ($LiAlH_4$) at 0 °C was slowly added a solution of 3.25 g (25.2 mmol) of 2-trideuteriomethyl-3-furoic acid (**8**) in 15 mL of dry ether. The mixture was stirred at room temperature for 10 h and a standard workup[34] gave 2.58 g (22.4 mmol; 89%) of 2-trideuteriomethyl-3-furylmethyl alcohol: IR (thin film) 3500 (br), 2250–2000, 1615, 1505, 1250, 1200, 1140, 1030, 985 cm$^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$ 7.24 (d, $J$ = 2.0 Hz, 1 H), 6.33 (d, $J$ = 2.0 Hz, 1 H), 4.44 (s, 2 H), 1.85 (br, 1 H). Without further purification 2.51 g (21.8 mmol) of the alcohol was converted to **2c** by using the procedure reported previously.[2] The benzoate was purified by column chromatography on silica gel (5% ether in hexanes) to yield 4.33 g (19.8 mmol; 91%) of **2c**: bp 104 °C (0.04 mmHg); IR (thin film) 1710, 1595, 1445, 1310, 1265, 1090, 1062 cm$^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$ 8.3–7.4 (m, 5 H), 7.27 (d, $J$ = 2.0 Hz, 1 H), 6.42 (d, $J$ = 2.0 Hz, 1 H), 5.17 (s, 2 H); $^{13}$C NMR ($CDCl_3$) $\delta$ 166.34, 150.79, 140.44, 132.75, 130,21, 129.50, 128.20, 114.60, 111.51, 5.37; high-resolution mass spectrum, calculated for $C_{13}H_9D_3O_3$ 219.09748, measured 219.09750.

**2-Trideuteriomethyl-3-furylmethyl-*α*,*α*-*d*$_2$ Benzoate (2d).** A 3.51-g (27.2 mmol) quantity of 2-trideuteriomethyl-3-furoic acid (**8**) was reduced with 1 molar equiv of lithium aluminum deuteride, using the procedure described for the synthesis of 2-trideuteriomethyl-3-furylmethyl alcohol, to give 2.99 g (25.6 mmol; 94%) of 2-trideuteriomethyl-3-furylmethyl-$\alpha,\alpha$-$d_2$ alcohol: IR (thin film) 3500, 2250–2000, 1614, 1505, 1260, 1230, 1140, 1050, 990 cm$^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$ 7.26 (d, $J$ = 2.0 Hz, 1 H), 6.34 (d, $J$ = 2.0 Hz, 1 H), 1.92 (br, 1 H). The alcohol was converted to **2d** by using the procedure reported previously.[2] The benzoate was purified by column chromatography on silica gel (5% ether in hexanes) to yield 5.11 g (23.1 mmol; 90.2%) of **2d**: IR (thin film) 2260–2000, 1715, 1600, 1450, 1310, 1270, 1115, 1050 cm$^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$ 8.3–7.4 (m, 5 H), 7.27 (d, $J$ = 2.0 Hz, 1 H), 6.44 (d, $J$ = 2.0 Hz, 1 H); $^{13}$C NMR ($CDCl_3$) $\delta$ 166.39; 150.95, 140.50, 132.81, 130.26, 129.56, 128.25, 114.49, 111.51; high-resolution mass spectrum, calculated for $C_{13}H_7D_5O_3$ 221.11003, measured 221.11010.

**General Pyrolysis Procedure.** The furnace was maintained at temperatures ranging between 670 and 680 °C. A sample of the furylmethyl benzoate 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. 90–100 °C during the pyrolysis. A condenser cooled below 0 °C was inserted between the furnace and the liquid-nitrogen-cooled trap to collect unreacted starting material and the benzoic acid formed as a byproduct. After the pyrolysis was completed, the liquid-nitrogen-cooled trap was warmed to −78 °C, and a known amount of a mixture of $CS_2$ and $CDCl_3$ at −78 °C was used to rinse the walls of the trap. Also added into the trap was a known amount of dibromoethane, used as an internal standard. After the product solution was transferred to NMR tubes at −78 °C, the NMR tubes were stored in liquid nitrogen ready for kinetic study. It should be noted that the solvents ($CS_2$ and $CDCl_3$) were deoxygenated, by freeze–thaw cycles, prior to use to prevent pyrolysis products from reacting with oxygen in the solvents.

**Procedure for Measuring the Rate Constants, *k*'s, of the Dimerization Reactions.** A JOEL FX-90Q NMR spectrometer equipped with a JNM-VT-3C variable-temperature controller was used to record the $^1$H NMR spectra of the pyrolysis products of the 2-methyl-3-furylmethyl benzoates **2a–d** at temperatures ranging between −55 and 0 °C. Temperatures were monitored by using a methanol standard[35] supplied by Varian. An NMR tube containing the pyrolysis products was kept in the NMR sample probe at a given temperature for about 7 h during which time 8 to 10 spectra were recorded. Spectra were rejected unless temperature readings, before and after each run of recording, were the same. Concentrations of monomer and dimer from each spectrum were calculated on the basis of added dibromoethane standard and from an average of 5 integrations. The rate constant, $k$, of the dimerization reaction was then calculated from the rate of disppearance of monomer as described above.

**Pyrolysis of 2-Methyl-3-furylmethyl Benzoate (2a).** For kinetic study, a quantity of about 300 mg (1.39 mmol) of **2a** was pyrolyzed each time at 670–680 °C and $10^{-4}$ Torr. The pyrolysate was collected in 3.0 mL of 1:1 $CS_2/CDCl_3$ from the liquid-nitrogen-cooled trap, and $^1$H NMR spectral data were recorded at low temperature for **1a**: $^1$H NMR (1:1 $CS_2/CDCl_3$) $\delta$ 6.76 (m, 1 H), 5.78 (m, 1 H), 5.23 (m, 1 H), 4.94 (s, 1 H), 4.84 (m, 1 H), 4.65 (m, 1 H) [lit.[2] $^1$H NMR (1:1 $CS_2/CDCl_3$) $\delta$ 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)]. In the temperature range of −50 to −15 °C, **1a** was slowly but quantitatively converted to **3a** (see Figure 1): $^1$H NMR (1:1 $CS_2/CDCl_3$) $\delta$ 7.15 (d, $J$ = 2.0 Hz, 2 H), 6.07 (d, $J$ = 2.0 Hz, 2 H), 3.05 (s, 4 H), 2.79 (s, 4 H) [lit.[2] $^1$H NMR ($CDCl_3$) $\delta$ 7.12 (d, $J$ = 2.0 Hz, 2 H), 6.05 (d, $J$ = 2.0 Hz, 2 H), 3.00 (s, 4 H), 2.74 (s, 4 H)]. Quantitative $^1$H NMR analysis using a dibromoethane standard indicated that pyrolysis of **2a** gave **1a** in 60% yield and the conversion of **1a** to its [4 + 4] dimer **3a** was greater than 98%.

**Pyrolysis of 2-Methyl-3-furylmethyl-*α*,*α*-*d*$_2$ Benzoate (2b).** For kinetic study, a quantity of about 300 mg (1.38 mmol) of **2b** was pyrolyzed each time at 670–680 °C and $10^{-4}$ Torr. The pyrolysate was collected in 3.0 mL of 1:1 $CS_2/CDCl_3$, and $^1$H NMR spectral data were recorded at low temperature for **1b**: $^1$H NMR (1:1 $CS_2/CDCl_3$) $\delta$ 6.76 (d, $J$ = 2.7 Hz, 1 H), 5.79 (m, 1 H), 4.84 (d, $J$ = 2.7 Hz, 1 H), 4.66 (m, 1 H) [lit.[2] $^1$H NMR (1:2 $CS_2/CDCl_3$) $\delta$ 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)]. Compound **1b** then dimerized quantitatively to **3b** (see Figure 4): $^1$H NMR (1:1 $CS_2/CDCl_3$) $\delta$ 7.15 (d, $J$ = 2.0 Hz, 2 H), 6.07 (d, $J$ = 2.0 Hz, 2 H), 3.05 (s, 4 H) [lit.[2] $^1$H NMR (1:2 $CS_2/CDCl_3$) $\delta$ 7.05 (d, $J$ = 2 Hz, 2 H), 6.00 (d, $J$ = 2 Hz, 2 H), 3.0 (s, 4 H)]. Quantitative $^1$H NMR analysis indicated that pyrolysis of **2b** gave **1b** in 55% yield and greater than 98% of **1b** was then converted to **3b**.

**Pyrolysis of 2-Trideuteriomethyl-3-furylmethyl Benzoate (2c).** For kinetic study, a quantity of about 300 mg (1.37 mmol) of **2c** was pyrolyzed each time at 670–680 °C and $10^{-4}$ Torr. The pyrolysate was collected in 3.0 mL of 1:1 $CS_2/CDCl_3$, and $^1$H NMR spectral data were recorded at low temperature for **1c**: $^1$H NMR (1:1 $CS_2/CDCl_3$) $\delta$ 6.76 (m, 1 H), 5.78 (m, 1 H), 5.23 (m, 1 H), 4.96 (s, 1 H). Quantitative analysis indicated that pyrolysis of **2c** gave 56% yield of **1c**, which then dimerized quantitatively to **3c** (see Figure 5): $^1$H NMR (1:1 $CS_2/CDCl_3$) $\delta$ 7.15 (d, $J$ = 1.7 Hz, 2 H), 6.08 (d, $J$ = 1.7 Hz, 2 H), 2.78 (s, 4 H).

**Pyrolysis of 2-Trideuteriomethyl-3-furylmethyl-*α*,*α*-*d*$_2$ Benzoate (2d).** For kinetic study, a quantity of about 200 mg (0.905 mmol) of **2d** was pyrolyzed each time at 670–680 °C and $10^{-4}$ Torr. The pyrolysate was collected in 3.0 mL of 1:1 $CS_2/CDCl_3$, and $^1$H NMR spectral data were recorded at low temperature for **1d**: $^1$H NMR (1:1 $CS_2/CDCl_3$) $\delta$ 6.76 (d, $J$ = 2.9 Hz, 1 H), 5.78 (d, $J$ = 2.9 Hz, 1 H). The pyrolysis of **2d** was found to give 52% yield of **1d**, which then dimerized quantitatively to **3d** (see Figure 6): $^1$H NMR (1:1 $CS_2/CDCl_3$) $\delta$ 7.15 (d, $J$ = 2.0 Hz, 2 H), 6.08 (d, $J$ = 2.0 Hz, 2 H).

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**Registry No.** **1a**, 73567-98-3; **2c**, 101980-33-0; **2d**, 101980-34-1; **6**, 101980-35-2; **7**, 101980-36-3; **8**, 101980-37-4; deuterium, 7782-39-0.

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