

## A Comparison of Reaction Kinetics Observed under Microwave Irradiation and Conventional Heating

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Kinetic studies were made of two reactions under microwave heating and under conventional heating. The reactions were the acid-catalyzed isomerization of carvone to carvacrol and the Diels-Alder reaction between anthracene and diethyl maleate. It was found that the rates of these reactions were the same, within experimental error, under either mode of heating at the same temperature. The activation parameters for the isomerization were measured as  $E^{\ddagger} = 89 \pm 3$  kJ/mol,  $\ln A = 21.5 \pm 0.8$  (oil bath); and  $E^{\ddagger} = 83 \pm 5$  kJ/mol,  $\ln A = 19.7 \pm 1.6$  (microwave). The activation parameters for the Diels-Alder reaction were  $E^{\ddagger} = 94 \pm 10$  kJ/mol,  $\ln A = 15.6 \pm 2.3$  (oil bath); and  $E^{\ddagger} = 88 \pm 8$  kJ/mol,  $\ln A = 13.9 \pm 2.0$  (microwave).

### Introduction

There has been increasing interest in the application of microwave irradiation to chemical reactions over recent years.<sup>1-3</sup> This activity also has been accompanied by speculation about the influence of microwaves on reaction rates. There have been reports of reactions which proceed faster in a microwave environment than under conventional conditions at the same temperature.<sup>4-8</sup> Other reactions have been reported to proceed at equal rates under both microwave and conventional heating at the same temperature.<sup>9-11</sup>

Perhaps the major reason for these conflicting interpretations lies with the technical difficulties associated with the application of microwave technology to chemistry. Conducting kinetics studies under microwave conditions is not a straightforward task. Although domestic microwave ovens are inexpensive and readily available, the multimodal cavity and duty cycle power application produce nonuniform heating<sup>9,12</sup> which can cause complications in chemical reactions. Consequently, the developed thermal gradients, along with the difficulty of measuring the temperature inside a microwave cavity, can lead to kinetics measurements that may not be valid. We have overcome these difficulties by substantially modifying a domestic microwave oven so that the applied microwave power can be held constant at a selected power level up to 750 W. The unit has been equipped with a magnetic

stirring device<sup>13</sup> and the reaction vessel fitted with a pressure gauge and an optic fiber thermometer.<sup>12</sup> Although the microwave field may not be homogeneous throughout the reaction vessel, we have demonstrated that solutions can be heated with stirring, without developing significant thermal gradients.

We have recently used this reactor to indicate that the acid-catalyzed esterification of 2,4,6-trimethylbenzoic acid in *i*-PrOH proceeded at the same rate regardless of whether the reaction was carried out in our microwave reactor or in an oil bath.<sup>11</sup> In that study we measured the activation parameters of the reaction during conventional heating and then used these values to calculate the extent to which the reaction should proceed over designated temperatures and times. The measured ester concentrations from the microwave experiments were in agreement with those predicted.

To firmly establish these preliminary findings it was necessary to experimentally determine reaction kinetics under both microwave and conventional heating conditions. In the present work experiments were conducted at constant temperature in both an oil bath and a microwave environment. Measurements of the rate constants at several temperatures allowed the activation parameters to be calculated and directly compared. The reactions investigated were the acid-catalyzed isomerization of carvone to carvacrol and the Diels-Alder cycloaddition between anthracene and diethyl maleate.

### Results

Sattar, Ahmad, and Khan have shown that when carvone is heated in the presence of acid it isomerizes to carvacrol.<sup>14</sup> This reaction was investigated because, in contrast with the Diels-Alder reaction also studied here, it involves a sequence of steps and a complex reaction mechanism yet still gives predominantly one product. The published method<sup>14</sup> involves conventional heating of a heterogeneous mixture; however, in order to facilitate the kinetics studies a homogeneous system was required. Eventually PhCl was chosen as solvent owing to a high dielectric constant which allowed it to absorb microwave radiation readily. TsOH was found to be a suitable acid when employed with 1,4-dioxane as a cosolvent.

- (1) Gedye, R. N.; Smith, F. E.; Westaway, K. C. *Can. J. Chem.* 1988, 66, 17.
- (2) Mingsos, D. M. P.; Baghurst, D. R. *Chem. Soc. Rev.* 1991, 20, 1.
- (3) Abramovitch, R. A. *Org. Prep. Proced. Intl.* 1991, 23, 683.
- (4) Sun, W. C.; Guy, P. M.; Jahngen, J. H.; Rossomando, E. F.; Jahngen, E. G. E. *J. Org. Chem.* 1988, 53, 4414.
- (5) Lewis, D. A.; Ward, T. C.; Summers, J. S.; McGrath, J. E. *Polym. Prepr. (Am. Chem. Soc. Div. Polym. Chem.)* 1988, 29, 174. Lewis, D. A.; Summers, J. D.; Ward, T. C.; McGrath, J. E. *J. Polym. Part A: Polym. Chem.* 1992, 30, 1647.
- (6) Bose, A. K.; Manhas, M. S.; Ghosh, M.; Raju, V. S.; Tabei, K.; Urbanczyk-Lipkowska, Z. *Heterocycles* 1990, 30, 741.
- (7) Berlan, J.; Giboreau, P.; Lefeuvre, S.; Marchand, C. *Tetrahedron Lett.* 1991, 32, 2363.
- (8) Adámek, F.; Hájek, M. *Tetrahedron Lett.* 1992, 33, 2039.
- (9) Jahngen, E. G. E.; Lentz, R. R.; Pesheck, P. S.; Sackett, P. H. *J. Org. Chem.* 1990, 55, 3406.
- (10) Pollington, S. D.; Bond, G.; Moyes, R. B.; Whan, D. A.; Candlin, J. P.; Jennings, J. R. *J. Org. Chem.* 1991, 56, 1313.
- (11) Raner, K. D.; Strauss, C. R. *J. Org. Chem.* 1992, 57, 6231.
- (12) Constable, D.; Raner, K.; Somlo, P.; Strauss, C. *J. Microwave Power and Electromagnetic Energy* 1992, 26, 195.

(13) A patent application has been lodged.

(14) Sattar, A.; Ahmad, R.; Khan, S. A. *Pak. J. Sci. Res.* 1980, 23, 177.

(15) White, J. R. *Trans. Intl. Microwave Power Inst.* 1973, 1, 40.

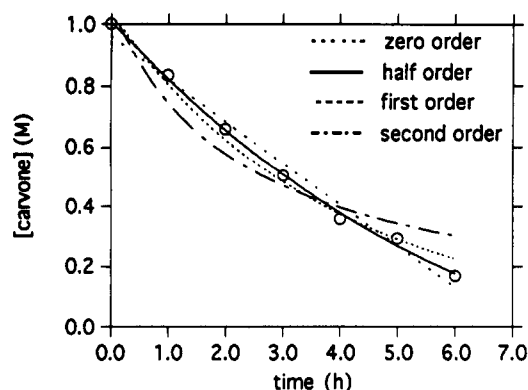
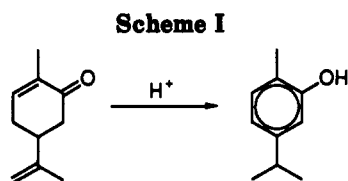


Figure 1. Isomerization of carvone at 150 °C under conventional conditions (oil bath):  $[\text{carvone}]_0 = 1.00 \text{ M}$ ,  $[\text{TsOH}] = 0.050 \text{ M}$ . The curves are the least-squares fits of eqs 2–5 (see text).



The rate equation had not been reported in the literature and so was determined empirically. In order to ascertain the orders  $n$  and  $m$  in eq 1, a series of reactions was performed under conventional conditions in an oil bath at different temperatures and at different acid concentrations.

$$-\frac{d[\text{carvone}]}{dt} = k[\text{carvone}]^n[\text{TsOH}]^m \quad (1)$$

Plots of  $[\text{carvacrol}]$  and  $[\text{carvone}]$  versus time showed that the rate equation is best described as half order with respect to carvone, i.e.,  $n = 1/2$ . The unexpected half order was a result of eq 1 being arbitrarily chosen as the form of the rate equation. However, the choice of  $n = 1/2$  gave an excellent fit to the data and was used for this work. Equations 2–5 are solutions to the differential equation 1 where  $[\text{TsOH}]$  has been regarded as constant. Figure 1 shows typical experimental data with fits for zero-order (eq 2), half-order (eq 3), first-order (eq 4), and second-

$$[\text{carvone}]_t = [\text{carvone}]_0 - k_{\text{obs}}t \quad (\text{derived from eq 1, } n = 0) \quad (2)$$

$$[\text{carvone}]_t = \left( \sqrt{[\text{carvone}]_0} - \frac{k_{\text{obs}}t}{2} \right)^2 \quad (\text{derived from eq 1, } n = 1/2) \quad (3)$$

$$[\text{carvone}]_t = [\text{carvone}]_0 e^{-k_{\text{obs}}t} \quad (\text{derived from eq 1, } n = 1) \quad (4)$$

$$[\text{carvone}]_t = \frac{1}{(k_{\text{obs}}t + 1/[\text{carvone}]_0)} \quad (\text{derived from eq 1, } n = 2) \quad (5)$$

$$k_{\text{obs}} = k[\text{TsOH}]^m \quad (6)$$

order kinetics (eq 5), with respect to carvone. The quality of each fit, expressed as the sum of the squares of the error

Table I. Quality of Fit for Various Models Describing the Kinetic Order, with Respect to Carvone, for Typical Experimental Data<sup>a</sup>

kinetic order	sum of squares error <sup>b</sup> (SSE)	correlation coefficient <sup>c</sup> ( $R^2$ )
zero order <sup>d</sup>	0.0085	0.9844
half order <sup>e</sup>	0.0011	0.9981
first order <sup>f</sup>	0.0069	0.9873
second order <sup>g</sup>	0.0397	0.9270

<sup>a</sup> Temperature 150 °C,  $[\text{carvone}]_0 = 1.00 \text{ M}$ ,  $[\text{TsOH}] = 0.050 \text{ M}$ . <sup>b</sup> SSE =  $\sum([\text{carvone}]_{i,\text{exptl}} - [\text{carvone}]_{i,\text{calc}})^2$ . <sup>c</sup>  $R^2 = 1 - n\text{SSE}/(n\sum[\text{carvone}]_{i,\text{exptl}}^2 - (\sum[\text{carvone}]_{i,\text{exptl}})^2)$  where  $n$  is the number of data points. <sup>d</sup> Equation 2. <sup>e</sup> Equation 3. <sup>f</sup> Equation 4. <sup>g</sup> Equation 5.

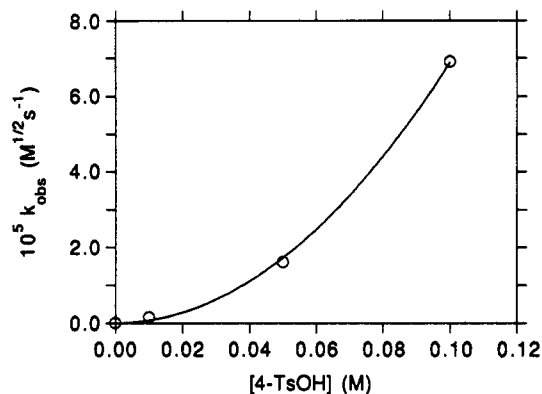


Figure 2. Rearrangement of carvone. Plot of the observed rate constant at different TsOH concentrations ( $[\text{carvone}]_0 = 1.00 \text{ M}$ ). The curve represents eq 6 with  $k = 6.89 \times 10^{-3} \text{ M}^{1/2} \text{ s}^{-1}$  and  $m = 2$ .

Table II. Kinetic Data for the Isomerization of Carvone under Catalysis by TsOH in PhCl/1,4-Dioxane (80:20)<sup>a</sup>

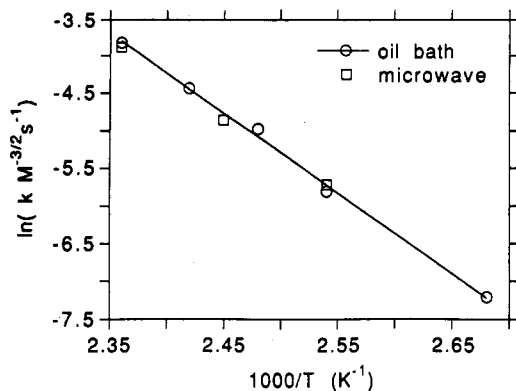
temp (°C)	[TsOH] (M)	microwave		oil bath	
		$k_{\text{obs}}^{b,c}$ ( $\text{M}^{1/2} \text{ s}^{-1}$ )	$k^{b,d}$ ( $\text{M}^{-3/2} \text{ s}^{-1}$ )	$k_{\text{obs}}^{b,c}$ ( $\text{M}^{1/2} \text{ s}^{-1}$ )	$k^{b,d}$ ( $\text{M}^{-3/2} \text{ s}^{-1}$ )
100	0.050			$1.8 \times 10^{-6}$	$7.2 \times 10^{-4}$
120	0.050	$8.2 \times 10^{-6}$	$3.3 \times 10^{-3}$	$7.5 \times 10^{-6}$	$3.0 \times 10^{-3}$
130	0.010			$1.6 \times 10^{-6}$	$6.9 \times 10^{-3}$
130	0.050			$1.6 \times 10^{-5}$	$6.9 \times 10^{-3}$
130	0.100			$6.9 \times 10^{-5}$	$6.9 \times 10^{-3}$
135	0.050	$2.0 \times 10^{-5}$	$8.0 \times 10^{-3}$		
140	0.050			$3.0 \times 10^{-5}$	$1.2 \times 10^{-2}$
150	0.050	$5.1 \times 10^{-5}$	$2.0 \times 10^{-2}$	$5.5 \times 10^{-5}$	$2.2 \times 10^{-2}$

<sup>a</sup>  $[\text{Carvone}]_0$  was 1.00 M. <sup>b</sup> Estimated uncertainty is  $\pm 10\%$ . <sup>c</sup>  $k_{\text{obs}}$  can be calculated by fitting eq 3 to a plot of  $[\text{carvone}]$  vs time or by fitting the equation  $[\text{carvacrol}]_t = [\text{carvone}]_0 - ([\text{carvone}]_0^{1/2} - k_{\text{obs}}(t/2))^2$  to a plot of  $[\text{carvacrol}]$  vs time. The tabulated values are the mean values determined by these two methods. <sup>d</sup> Calculated from eq 6 except for the value at 130 °C which was determined from a plot of  $k_{\text{obs}}$  vs  $[\text{TsOH}]$ .

(SSE) in the least squares regression and the correlation coefficients, is shown in Table I.

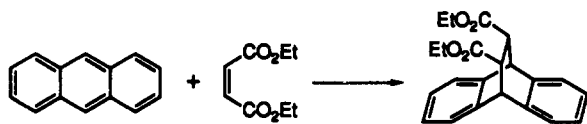
From the experiments carried out at the same temperature but with different acid concentrations, it was possible to determine the value of  $m$ . By fitting eq 3 to the data from such experiments the pseudo-half-order rate constants  $k_{\text{obs}}$  could be determined. A plot of  $k_{\text{obs}}$  versus  $[\text{TsOH}]$  was found to be quadratic indicating that  $m = 2$  (see Figure 2). Hence the reaction was second order with respect to TsOH.

After fitting eq 3 to the data from the above experiments it was possible to calculate  $k_{\text{obs}}$  and hence the actual rate constant  $k$  at various temperatures (Table II) and to construct an Arrhenius plot (Figure 3). The  $E^*$  was determined as  $89 \pm 3 \text{ kJ/mol}$  and  $\ln A$  was  $21.5 \pm 0.8$ .



**Figure 3.** Plot of  $\ln k$  versus  $1/T$  for the isomerization of carvone. The line is the least-squares linear fit to the oil bath data.

### Scheme II



**Table III.** Second-Order Rate Constants for the Diels-Alder Reaction between Anthracene and Diethyl Maleate in 1,2-Xylene<sup>a</sup>

temp (°C)	microwave $k$ ( $M^{-1} s^{-1}$ )	oil bath $k$ ( $M^{-1} s^{-1}$ )
140	$1.0 \times 10^{-5}$	$9.6 \times 10^{-6}$
150	$1.5 \times 10^{-5}$	$1.3 \times 10^{-5}$
160	$3.5 \times 10^{-5}$	$2.9 \times 10^{-5}$
170	$4.7 \times 10^{-5}$	$4.4 \times 10^{-5}$
180	$8.8 \times 10^{-5}$	$1.0 \times 10^{-4}$

<sup>a</sup> At 140, 150, 160, and 170 °C [anthracene]<sub>0</sub> = 0.278 M, [diethyl maleate]<sub>0</sub> = 2.78 M; at 180 °C [anthracene]<sub>0</sub> = 0.166 M, [diethyl maleate]<sub>0</sub> = 1.66 M.

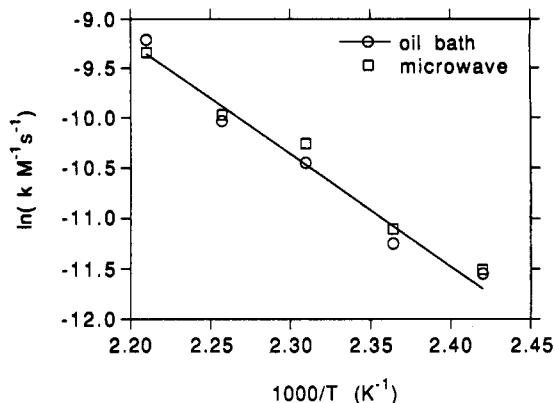
The isomerization was then studied in the microwave reactor. The concentrations of carvone and carvacrol were monitored at three temperatures, and the values of the rate constant  $k$  were determined (see Table II). An Arrhenius plot gave the  $E^{\ddagger}$  as  $83 \pm 5$  kJ/mol and  $\ln A$  as  $19.7 \pm 1.6$ . The data from these experiments are in excellent agreement with the data obtained in the conventional oil bath experiments as can be seen in Figure 3.

The Diels-Alder cycloaddition of anthracene and diethyl maleate has been reported to be more rapid under microwave irradiation than under conventional conditions, at the same temperature.<sup>7</sup> Because this recent result contrasted with our previous findings<sup>11</sup> and with the kinetics of isomerization of carvone to carvacrol discussed above, it warranted further investigation. We have measured rate constants at various temperatures under microwave and conventional conditions and found that the reaction proceeded slowly. Since anthracene has only limited solubility in 1,2-xylene, we increased the reaction rate by using a 10-fold excess of the ester. Under these conditions the concentration of the ester varied by less than 10% and hence the reaction was observed to proceed with pseudo-first-order kinetics as described by eq 8. The

$$-d[\text{anthracene}]/dt = k[\text{anthracene}][\text{diethyl maleate}] \quad (7)$$

$$[\text{anthracene}]_t = [\text{anthracene}]_0 e^{-k[\text{diethyl maleate}]t} \quad (8)$$

second-order rate constants  $k$  were calculated by fitting



**Figure 4.** Plot of  $\ln k$  versus  $1/T$  for the Diels-Alder reaction between anthracene and diethyl maleate. The line is the least-squares linear fit to the oil bath data.

eq 8 to the experimental data and are shown in Table III. An Arrhenius plot is shown in Figure 4, and from this the  $E^{\ddagger}$  and  $\ln A$  were measured as  $94 \pm 10$  kJ/mol and  $15.6 \pm 2.3$ , respectively.

The Diels-Alder reaction was then investigated in the microwave reactor. Plots of [anthracene] vs time were constructed, and from these the rate constants were calculated at various temperatures. The data are listed in Table III and displayed in the graph in Figure 4. The  $E^{\ddagger}$  was determined to be  $88 \pm 8$  kJ/mol and  $\ln A$  was  $13.9 \pm 2.0$ .

## Discussion

There are many mechanisms by which microwaves can heat,<sup>15</sup> perhaps the main one of relevance to organic solvents being dielectric heating. This involves the alignment of the dipoles of molecules with the electric field component of the radiation. In practice, the developed polarization vector lags behind the electric field vector and this causes the heating effect.<sup>16</sup> It should be noted that dipole alignment does not refer to the dipole rotations observed in spectroscopic transitions.

There appears to be a common misconception that microwave radiation at 2.45 GHz can excite rotational transitions. The microwave spectra of rigid linear molecules exhibit a series of evenly spaced absorption lines with frequencies given by

$$\nu_{J \rightarrow J+1} = 2B(J+1) \quad J = 0, 1, 2, \dots$$

where  $B$  is a rotational constant and  $J$  is the rotational quantum number. The lowest frequency absorption line is at  $2B$ . The rotational spectra of rigid symmetric tops exhibit the same pattern of absorption lines. Generally, the frequencies at which molecules undergo rotational transitions are well above the operating frequency of the domestic microwave oven (2.45 GHz). For example, the first absorption lines of OCS, CO, HF, and  $\text{CH}_3\text{F}$  occur at 12.2, 115, 1230, and 51 GHz, respectively.<sup>17</sup>

Internal bond rotations also require higher frequencies for excitation. Strictly speaking these "rotations" should

(16) Metaxas, A. C. *Industrial Microwave Heating*; Peregrinus: 1983.  
(17) Banwell, C. N. *Fundamentals of Molecular Spectroscopy*, 2nd ed.; McGraw-Hill: New York, 1972.

be referred to as torsional vibrations and are excited by IR radiation at ca. 100–400  $\text{cm}^{-1}$  (3000–12 000 GHz).<sup>18</sup>

The above arguments suggest that when a dipolar material is irradiated with microwave energy at 2.45 GHz, the heating effect is due to dielectric heating and the radiation does not directly excite the molecule to higher rotational or vibrational energy levels. However, the energy absorbed by the material will increase its internal energy. The internal energy will then be partitioned between translational, vibrational, and rotational energy *regardless* of the method of heating. Hence, one might expect no kinetic differences between microwave irradiated reactions and conventionally heated reactions. The results described here and previously<sup>10,11</sup> indicate that this is the case.

We believe that the earlier observations of nonthermal microwave effects probably resulted from inherent experimental difficulties relating to temperature measurement and/or the development of thermal gradients within the sample. For example, in an initial study of the kinetics of the hydrolysis of ATP, Jahngen et al.<sup>4</sup> concluded that the reaction proceeded at a faster rate under microwave irradiation than under conventional conditions at the same temperature. They<sup>9</sup> later found that it was crucial to consider the thermal gradients within the irradiated sample, and when they were able to carefully take these into account it became clear that there was no justification for assuming a kinetic effect.

Lewis et al.<sup>5</sup> and Berlan et al.<sup>7</sup> have both reported reactions to proceed faster under microwave irradiation. In each case the temperature in the sample was carefully measured with a fluoroptic thermometer. However, it is possible that these kinetic measurements may not be valid due to thermal gradients being created in their sample holders. In support of this interpretation, we have attempted here to duplicate the result obtained by Berlan et al.,<sup>7</sup> but found no acceleration in the rate of the reaction under microwave conditions.

### Experimental Section

NMR spectroscopy was performed on a 200-MHz spectrometer. GC was performed on an instrument fitted with a QS BP5 capillary column 25 m in length. Helium was used as the carrier gas at a flow rate of 2.0 mL/min. The oven was maintained at 50 °C for 2 min and was then heated at 10 °C/min to a final temperature of 280 °C. The final temperature was held for 10 min. All reactions were conducted in homogeneous solution.

(18) Flygare, W. H. In *Physical Methods of Chemistry*; Wiley-Interscience, New York, 1972; Vol. 1, Part IIIA. Lowe, J. P. In *Progress in Physical Organic Chemistry*; Wiley-Interscience, New York, 1968; Vol. 6.

Reactions in the microwave reactor<sup>12</sup> were magnetically stirred in a pressurized vessel and the temperature was monitored continuously.

**Isomerization of Carvone under Conventional Conditions.** Solutions of carvone (1.00 M) and TsOH (0.010, 0.050, or 0.100 M) in PhCl/1,4-dioxane (80:20) were prepared. Samples of these solutions (5 mL) were sealed in thick-walled glass tubes and were placed in an oil bath thermostated at the appropriate temperature. The tubes were withdrawn at intervals and were cooled and opened. A solution of 1,2,4,5-tetramethylbenzene (1.00 M, 0.5 mL) was added to a sample of the reaction mixture (0.5 mL). Pyridine (0.5 mL) and  $\text{CHCl}_3$  (1.0 mL) were then added, and the solution was analyzed by GC. The retention times were as follows: 8.31 (1,2,4,5-tetramethylbenzene), 10.39 (carvone), and 11.22 min (carvacrol).

**Isomerization of Carvone under Microwave Irradiation.** Solutions of carvone (1.00 M) and TsOH (0.050 M) in PhCl/1,4-dioxane (80:20) were prepared. These solutions (75 mL) were added to a Teflon reaction vessel and placed in the microwave reactor. The microwave power was applied, and the solution was heated to the desired reaction temperature. After the appropriate time the microwave power was turned off to allow the reaction solution to cool. The cooling was hastened by an ice bath. The reaction mixture was analyzed by GC as described above.

**Diels-Alder Reaction of Anthracene with Diethyl Maleate under Conventional Conditions.** Samples of anthracene (0.220 g, 1.24 mmol or 0.110 g, 0.62 mmol), diethyl maleate (2.10 g, 12.2 mmol or 1.05 g, 6.1 mmol), and 1,2-xylene (2.0 mL) were added to thick-walled glass tubes. The tubes were sealed and were placed in a thermostated oil bath. After the appropriate time the tubes were withdrawn, the liquid level was recorded, and the contents were allowed to cool. The tubes were then opened, and the contents were dissolved in  $\text{CH}_2\text{Cl}_2$  (30 mL). A small sample (1 mL) of this solution was evaporated to dryness at room temperature on an oil pump. The ratio of the adduct to anthracene was then determined by  $^1\text{H}$  NMR spectroscopy. On occasion hexamethylbenzene was added after the reaction as an internal standard. However, this was not essential for quantification as the reaction proceeded cleanly without byproduct formation. The initial concentrations of the reagents in the reaction mixture were calculated from the recorded liquid level.

**Diels-Alder Reaction of Anthracene with Diethyl Maleate under Microwave Irradiation.** Samples of anthracene (4.40 g, 24.7 mmol or 2.75 g, 15.4 mmol), diethyl maleate (42.00 g, 24.4 mmol or 26.25 g, 15.3 mmol), and 1,2-xylene (40 or 50 mL) were added to a Teflon reaction vessel. The microwave power was applied, and the solution was heated to the desired reaction temperature. After the appropriate time the microwave power was turned off to allow the reaction solution to cool. The cooling was hastened by an ice bath. The reaction mixture was analyzed by NMR as described above.

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